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OF THE

## AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Volume 191

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INSTITUTE OF METALS DIVISION, IRON  
AND STEEL DIVISION, AND EXTRACTIVE METALLURGY  
DIVISION

1951

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PAPERS AND DISCUSSIONS PRESENTED AT MEETINGS HELD AT NEW  
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## FOREWORD

This, the 191st volume of the Transactions of the American Institute of Mining and Metallurgical Engineers, contains the technical papers of the three Divisions of the Metals Branch published in the Transactions section of the JOURNAL OF METALS in 1951. As initiated in volume 185 and continued in volume 188, the technical papers and discussions of the Institute of Metals, Iron and Steel, and Extractive Metallurgy Divisions are presented under a single cover.

Most of our members are aware of the rather stringent financial circumstances surrounding publication activities of the Institute and especially of the Metals Branch. Substantial progress has been made in ameliorating these difficulties, and particularly in the emergence and growth of the JOURNAL OF METALS with greater advertising revenue.

Papers published in this volume derive from a period of acute retrenchment in the Branch publishing program. They represent the distillate of the distillate. The work of the Divisional publications committees has been arduous in an effort to avoid eliminating any valuable papers, to eliminate any unnecessary wordage or information already available elsewhere, to encourage the submission of shorter papers or technical notes by authors only part of whose work was new or conclusive, and to strive for clarity in the final version of every paper accepted for publication. All readers owe these committees a debt of gratitude.

The Institute of Metals Division, which has suffered the greatest disparity between material available and that for which publication space could be found, has contributed 74 papers. High technical quality of the work will be evident to the reader. The Institute of Metals Division Lecture by Borelius is included in this group.

The Iron and Steel Division is represented by a group of 15 papers ranging from thermodynamics to plant operations. The Howe Memorial Lecture by Vilella is included in this group.

The Extractive Metallurgy Division presents 19 papers. It is particularly encouraging to note the contributions dealing with physical chemistry. Description of plant operations, a subject vital to the quickened professional growth of young engineers, has received modest attention and merits more as Institute income increases and more papers become available.

An expression of thanks and appreciation is due the authors and discussion contributors. We must express our appreciation to the members of the headquarters staff, to the Division officers, and to the members of the various Divisional committees, without whose cooperative efforts this volume could not have come into existence. Finally, we of the metallurgical profession must express our thanks to those companies and institutions which have donated the time required by their author and committee members for preparation of the solid contribution to the literature represented by Volume 191.

DECEMBER 3, 1951  
JOSEPHTOWN, PA.

CARLETON C. LONG, *Chairman*  
Metals Branch Council, AIME

JOURNAL OF METALS was paged consecutively throughout 1951. Thus, in this volume of the Metals Transactions there are 11 interruptions in the pagination. The missing pages appeared in JOURNAL OF METALS. This volume consists of all the Metals Transactions for 1951.

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# Industrial Hygiene At American Smelting and Refining Company

by John N. Abersold and K. W. Nelson

**I**NDUSTRIAL hygiene has been defined by Patty<sup>1</sup> as "the science and art of recognizing, evaluating, and controlling potentially harmful factors in the industrial environment." This definition implies thorough study of operations, evaluation of potentially harmful factors through air sampling, micro-analyses and other means, and, finally, appropriate medical and engineering control wherever indicated.

The prevention of industrial health injuries is a vital part of operations of American industry today. Progress and interest in this field has increased steadily for many years, the most rapid progress having been attained, perhaps, during the last three decades. It is significant to note that there are now official agencies in 46 states actively concerned with industrial health problems and that a western field station has been established recently in Salt Lake City by the U. S. Public Health Service to augment its industrial hygiene services directed from headquarters of the National Institute of Health, Bethesda, Md. Many of the larger industries have found it advantageous to establish their own industrial hygiene departments.

The American Smelting and Refining Co. is a world-wide organization engaged in the mining, smelting, and refining of lead, copper, zinc, silver, gold, by-product metals, including cadmium, arsenic, and others. In the United States there are 13 smelters and refineries, 11 secondary smelters or foundries, and a number of mines. Approximately 9000 workers are normally employed.

It has long been the established company policy to seek out occupational hazards and provide safeguards for employee health. Protective equipment has been supplied to individual workers and exhaust ventilation installations have been in use in some operations for more than 40 years. All of the major units have their own medical departments which provide employees with excellent medical and hospital care.

In 1937 full scale industrial hygiene studies were undertaken at the Selby Plant and were extended to most of the other smelters during the next three years. In 1945 the Department of Hygiene was organized with Professor Philip Drinker of Harvard University as Director and with Dr. S. S. Pinto as Medical Director. The department is responsible for coordinating and maintaining a program for the good health of all employees from top management down to the lowest paid day worker. It is essentially a service organization serving all of the United States plants regardless of location or size. Full and part-time physicians employed in all of the company's American plants and working in close cooperation with the Medical Director are responsible for de-

termining the state of health of all the employees and giving treatment when necessary. In general, medical care is confined to accidents or illnesses occurring while the men are on the job. Among the duties of the doctors is the making of careful physical examinations of new employees and routine check-ups of old employees.

In addition to medical care a primary responsibility of the department is the *prevention* of occupational illnesses. In this the main concern is with the working environment in relation to its effect on the worker. Environmental factors may be dusts, fumes, gases, toxic materials, heat, humidity, radiation, or noise. The objectives are: (1) Immediate control of these factors through the education of the worker, through providing the wearing of respirators or other protective devices, and through careful medical examinations and regular analysis of urine specimens; (2) a long range control program which may be accomplished by local exhaust ventilation, wetting of materials, changes in metallurgy, changes in methods of handling, or by use of special devices and special equipment.

To accomplish these objectives a fine industrial hygiene laboratory was built in Salt Lake City and equipped to do routine and experimental work. Trained and experienced industrial hygienists obtain the facts by making frequent hygiene surveys. These surveys include tests of the air, studies of all processes, and careful investigation of ventilation, lighting, and general working conditions. Except in emergencies, the air contaminants and often the substances handled by the worker are sent to the laboratory for analysis by chemists and technicians specially trained in industrial hygiene methods. The findings are evaluated in terms of limits recommended by various State and Federal agencies, and in light of all available medical data.

The methods used for studying the working environment involve all of the usual chemical and physical procedures employed in industrial hygiene. The Impinger, electric precipitator, thermal precipitator, and filter paper sampler have been used to collect atmospheric dust and fume samples. Of special interest here is the filter paper sampler, shown in Fig. 1, which was developed by Dr. Silverman at Harvard University. The instrument has been improved and is used very extensively in field studies. A water manometer connected behind an orifice is used to determine the rate of air flow. Calibration is effected by use of a standard gas meter or rotameter. The dust or fume is collected on a filter paper clamped between two rings, as shown in Fig. 2. The filter paper, such as Whatman No. 52, collects both dust and fume with a very high efficiency. The instrument is very convenient and easily transported.

The solids collected on the filter paper are analyzed in the laboratory usually by use of a polarographic procedure. By this procedure it is possible to measure quantitatively in a single analysis the

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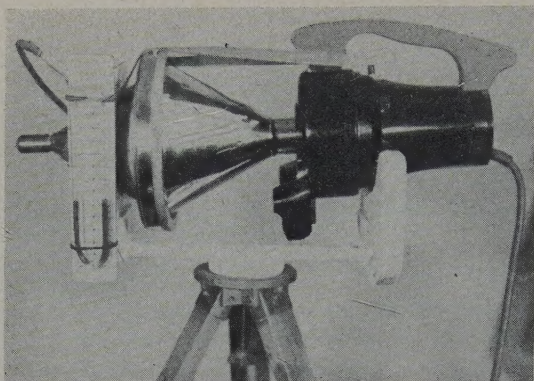


Fig. 1—Filter paper sampling apparatus ready for use.

copper, lead, cadmium, and zinc in each sample. Polarographic methods are also used for the determination of a number of other elements.

Dusts of various types are the most common contaminants found in the atmosphere of the various plants. Fumes containing lead oxide may be found in certain smelter and refinery work areas and are given special attention since lead oxide is more readily absorbed than other less soluble lead compounds, such as the sulphide. Other contaminants such as carbon monoxide, hydrogen sulphide, sulphur dioxide, selenium, tellurium, cadmium, and arsenic may be found and require study. Certain of the gases mentioned may be toxic or irritant. In order to be constantly on the alert and to be warned in advance, rapid field tests have been developed for hydrogen sulphide, chlorine, and arsine from a basic British method. In this method a small hand pump is used to draw air through filter paper disks impregnated with various reagents which produce a stain if traces of gas are present, see Fig. 3. These stains are compared with standards to estimate the gas concentrations. By use of this method chemists and safety directors are able to check the working environment for suspected dangers. For one plant where hydrogen sulphide is being used in one of its operations, a machine is being developed to sound automatically an alarm before any escaping gas reaches dangerous concentrations.

From time to time certain analyses requiring highly specialized training or very expensive equipment are performed by the research laboratory or outside laboratories; for example, spectrographic and petrographic analyses. Certain types of research work involving animal experimentation have been performed through grants to Harvard University.

As a part of the fact-finding function of the Hygiene Department, urine specimens and frequently blood specimens are obtained from all workers exposed to lead and other metals and examined at



Fig. 2—Sampling apparatus unassembled.

the Hygiene Laboratory. These tests indicate what the worker has been breathing, usually long before illness occurs. During the past year more than 5000 determinations for lead in urine were made. On the basis of these and other medical findings, the Medical Director may make recommendations for immediate protection of the employee.

The evaluation of all findings is an important function of the Hygiene Department. This involves in part an appraisal of air studies and the correlation of these studies with medical data. When all the facts are brought together, an overall evaluation of the environment is made, the need for control measures determined, and a coordinated control program outlined. Recommendations for control are made to the plant manager and passed on to engineers especially trained in industrial hygiene ventilation. The plant manager and the superintendent with his operating staff decide what method of control should be carried out. This is logical because control may be accomplished by changes

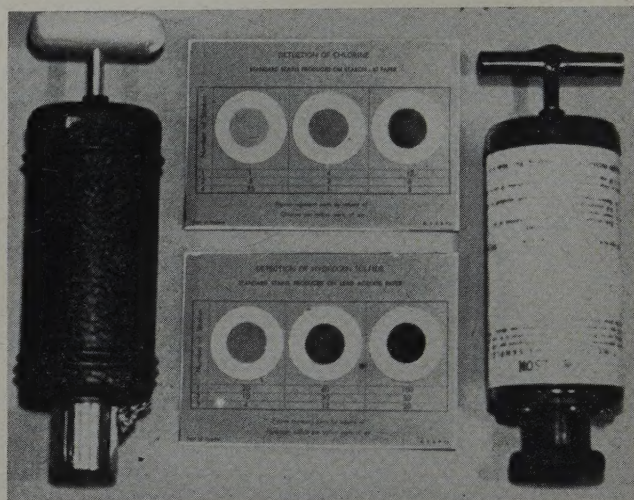


Fig. 3—Sampling pumps and standard stains for field determinations of hydrogen sulphide and chlorine.

in metallurgy or methods of handling rather than by local exhaust ventilation or other engineering or chemical means. Occasionally control is not possible by engineering means and it is necessary to rely on respiratory protective devices and medical control procedures. Sometimes the recommendations for plant improvements are based on comfort alone rather than a health hazard.

The ventilation engineers form a unit or a division of the Western Engineering Department but work in the closest cooperation with the Hygiene Department in carrying out the detailed recommendations. Frequent conferences are held with these engineers and general plans are approved.

### Plant Improvements

Elimination or control of all potentially harmful factors in the environment is the major long-range objective. Since 1938, and particularly during the past four years, much progress has been made toward this objective. In some cases, such as in the mills, the cost has been very high—from ten to twenty thousand dollars per worker. Following are some of the highlights of control of dusts, fumes, and gases in the various plants achieved through the combined interest and effort of managers, superintendents, metallurgists, foremen, the specially trained staff of ventilation engineers of the Western



Engineering Department and the Department of Hygiene:

**Mills:** Wetting has long been used to control dusts in mills. However, because wetted materials in some cases clog up screens and chutes and hinder proper cleaning of equipment between ore lots, other means of control have had to be used also, chiefly local exhaust ventilation and dust collection by small bag-house units and centrifugal impingement washers. Because of the very high cost, experimental work has been conducted to find other methods. Mist-sprays produced by atomizing water with compressed air have been tried. The minute droplets of water produced by these sprays actually wet dust particles and help to reduce the escape of dusts at the source, yet they avoid objectionable wetting of the flowing material. With this method of control a 50 pct reduction in dust concentrations has been achieved in one mill.

In certain instances protection of the worker has been accomplished by ventilating and air conditioning small areas where men work, such as crane cabs, when the general ventilation of the room would be difficult if not impossible, see Stevenson.<sup>2</sup> In other words, the man has been "ventilated" instead of the operation. Cabs of cranes handling ores, carrying hot metals over furnaces, etc., are examples. This approach is being tried now in mills by building booths kept under positive pressure with filtered air for workers whose duties can be carried out from such an enclosure.

**Sampling Rooms:** Local exhaust ventilation and good housekeeping have been used exclusively to control dusts in sampling rooms, see Fig. 4. Modern grinding and sampling equipment are easily enclosed and the dust can be controlled at a very moderate cost.

**Beds and Charge Bins:** Wetting, enclosure and local exhaust ventilation are being used for control of dusts in such equipment. Dust control in these departments is one of the most difficult problems. Wetting can only be used to a limited degree because excess moisture may affect the roasting of certain types of charges.

The unloading of truckloads of ores and concentrates for storage or making up charges was a difficult problem to control in one plant. The final solution was found in a semi-enclosure and hood with high volume air intake.



Fig. 4—Ore sample being screened at bucking table with use of exhaust ventilated hood.

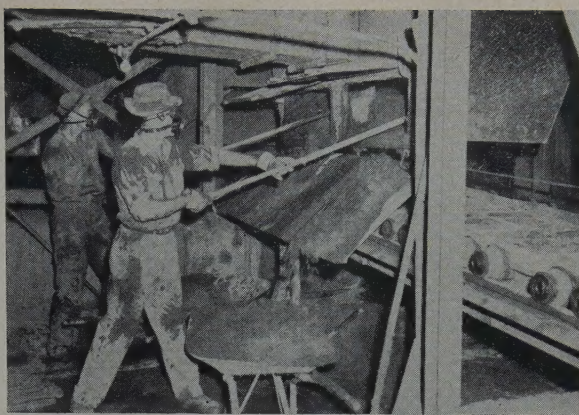


Fig. 5—Workers removing wetted dust from wind boxes of a first-over Dwight-Lloyd sinter machine.

**Dwight-Lloyd Sinter Plants:** Wetting, enclosure and local exhaust ventilation have been the principal methods of controlling dust and fume in the Dwight-Lloyd sinter plants. Water may be added to both first and second-over charges at the belt tripper, at the mixing tables and sometimes with use of pug-mills. Water is used to quench the sinter after it is roasted and the discharge ends of the machines are kept tightly enclosed.

The control of dusts from crushing first-over sinter has been effected with local exhaust ventilation and collection of dusts with centrifugal impingement washers.

The dustiest Dwight-Lloyd operation is the removal of deposits from wind boxes. Control of these dusts has been effected by (1) use of enclosed pan or screw conveyor along wind boxes with draft maintained on the boxes, (2) wetting by inserting into the dust piles a water pipe with flowing water and (3) maintenance of a water seal in the bottom of the wind boxes which completely wets the accumulating dusts. In Fig. 5 is shown the absence of visible dusts after wetting with inserted water pipes. The water seal has been applied only to second-over machines.

Good housekeeping with frequent wash down of floors is very important in control of dusts. Thermal air currents plus vibration can redisperse settled dusts.

Considerable improvement in dust and fume concentrations was effected in one Dwight-Lloyd plant by a change in metallurgy, that is, a lowering of the percentage of coke in the charge.

Excessive heat has been controlled by insulating wind boxes and air ducts and by use of large hoods mounted over the pallet immediately behind burners and connected to a stack for gravity ventilation.

**Lead Blast Furnaces:** The make up of blast furnace charges may involve dusty operations if the second-over sinter is not sufficiently wetted. The sinter is usually stored in hoppers and it has been found necessary to provide exhaust ventilation when the sinter is withdrawn.

The control of dust and fume at the feed to the blast furnace is accomplished chiefly by good draft on the furnace.

The lead blast furnace cannot be tapped for slag, or for lead if the temperature is high, without the generation of much lead fume. Fume from these points is controlled with local exhaust ventilation at all furnaces. It is necessary to raise and lower these hoods occasionally and workers have sometimes neglected this duty because of the little extra work



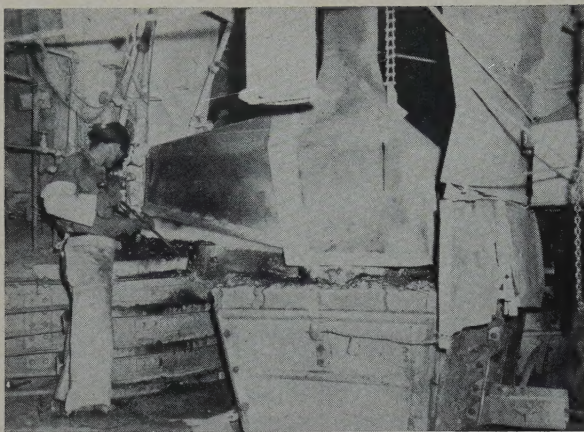


Fig. 6—Lead and slag being tapped from a blast furnace with use of an improved exhaust ventilated hood.

required. To overcome this and provide heavier construction to resist the heat, a hood has been very recently designed which can be raised and lowered by an electric motor merely by pressing a button as shown in Fig. 6. Stand-by empty or filled lead pots sometimes cause considerable fume. To control this an exhaust ventilated hood with a flexible fireproof duct has been developed.

**Reverberatory Furnaces:** Control of dust and fume from operation of lead dross reverberatory furnaces has been effected by adequate draft on furnaces to prevent escape of fume at the charge door and by local exhaust ventilation at the tap holes and launders for speiss and matte.

**Kettles:** One of the most difficult problems has been control of dusts and fume from refining operations in kettles. Complete or partial hoods with exhaust ventilation have been effective where metals are transferred to kettles or when stirring is done to separate drosses. Fig. 7 shows a partial hood with a high volume air intake to control the fume over the surface of a lead kettle. As another approach to reducing dustiness during dross skimming, experimental work is now under way to (1) change the metallurgy, (2) remove drosses with a screw-type conveyor with local exhaust ventilation at point of discharge into skip and (3) use of a high velocity slot type exhaust around edge of kettle. A fair degree of success has been achieved with use of the screw-type conveyor.

**Flues:** The removal of settled dusts from flues has

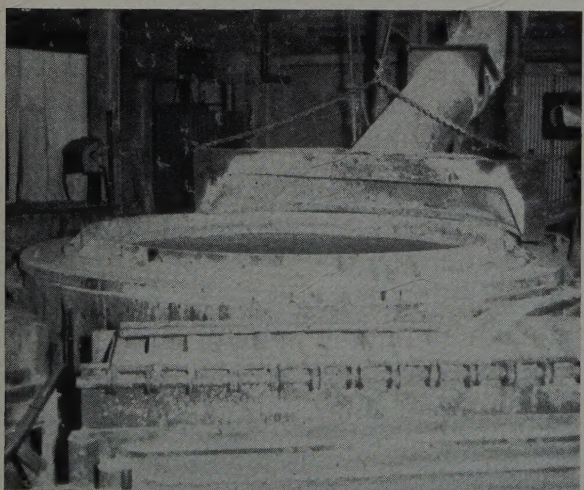


Fig. 7—Partial hood with high volume air intake over a lead kettle for control of lead fume.

long been a dusty and unhygienic operation. To control the dusts from this operation, engineers and metallurgists from the Federal Plant<sup>3</sup> developed the telescopic tube device shown in Fig. 8. This device serves as an enclosure and wetting chamber combined. A circular water spray located near the top partially wets the dusts as they pass from flue to car. The wetting of the dusts is continued in the car and minimizes dusting in later handling.

**Cottrells:** The control of atmospheric dusts resulting from the cleaning of cottrell hoppers has been difficult. Enclosed and ventilated conveyors along hoppers have not been adequate. Spills which create airborne dusts do occur in spite of the best care. The problem has finally been solved by replacing the workers with automatic equipment. Electric vibrating hammers have now been installed on most of the cottrell units.

**By-Products Metals:** The control of dusts and gases in the refining and packaging of by-product



Fig. 8—Workmen extracting flue dust with use of telescopic tube device designed for control of dusts by wetting and enclosure.

elements, such as selenium, tellurium, and cadmium, has been accomplished by use of local exhaust ventilation almost exclusively.

The hygiene program and some of the work that has been done to improve working conditions in the American Smelting and Refining Co. have been reviewed briefly. In presenting this information there is no wish to convey the impression all objectives have been reached. There are problems yet to solve, and changes in operations and new processes continually arise which require study and control. In one smelter recently the minutest details of control in a new process were worked out before the plant was built in order that no chances would be taken. Top management and operating staffs displayed keen interest and cooperated to the fullest extent. The same interest and cooperation from managements of all plants have existed in all other phases of the industrial hygiene program and are largely responsible for what measure of success has been achieved.

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- <sup>1</sup> F. A. Patty: American Industrial Hygiene Assoc. Quarterly. (Sept. 1946) 7, No. 3, p. 3.
- <sup>2</sup> B. R. Small, with supplement by C. A. Stevenson: Air Conditioned Crane Cabs. Engineering Series publication by Industrial Hygiene Foundation of America. Mellon Institute, Pittsburgh, Pa. 1946.
- <sup>3</sup> Federal Plant, American Smelting and Refining Co., Alton, Ill.; Luther J. Buck, Manager.



# Solution Loss and Reducing Power Of Blast Furnace Gas

by T. L. Joseph

A study is made of the amount of solution loss necessary to maintain the reducing power of the gas stream in the blast furnace. Curves are presented to show the effect of solution loss, moisture in the blast, and carbon dioxide from the flux on the nitrogen in the top gas.

THE blast furnace process is based upon the counter flow of gases and solids. As CO, N<sub>2</sub> and H<sub>2</sub> flow upward from the combustion zones, oxygen is acquired from the descending charge. In the reduction of iron ore, a portion of CO is converted to CO<sub>2</sub> and similarly a portion of H<sub>2</sub> is converted to water vapor. The inert N<sub>2</sub>, from the air used in combustion, passes through the furnace with little change. Its concentration is, however, decreased by reactions such as direct reduction and solution loss which increase the volume of CO in the gas stream. Similarly the evolution of CO<sub>2</sub> from the limestone also dilutes the nitrogen.

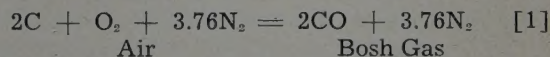
The purpose of this paper is to illustrate an idealized and simplified method of studying furnace processes by following changes in the gas phase between the tuyeres and the stock line. A more specific objective is to evaluate the effect of solution loss upon the CO/CO<sub>2</sub> ratio in that region of the furnace in which FeO is reduced to metallic iron. This last stage of reduction requires relatively high CO/CO<sub>2</sub> ratios to exceed the equilibrium requirements. Solution loss or the reaction of CO<sub>2</sub> with C to produce CO has a pronounced effect upon the ratio of the carbon gases and is necessary to maintain the reducing power of the gas stream if the consumption of coke is low. It will be explained later that indirect reduction followed by solution loss is stoichiometrically equivalent to direct reduction.

Calculations will be made to show how the composition of the gas in the region of the mantle varies with coke consumption and with different amounts of solution loss. Such calculations show the condi-

tions under which gasification of C with oxygen in the charge is needed to maintain the reducing power of the gas. Equilibrium conditions for FeO and the carbon gases will be used to establish a minimum CO/CO<sub>2</sub> ratio below which reduction will not proceed. The manner in which carbon is gasified in the furnace, at the tuyeres with oxygen in the air or above the tuyeres with oxygen from the charge, will be a basic feature of all calculations. It is hoped that greater interest in the use of top gas as a means of following furnace reactions will be aroused by the calculations and generalized curves which are presented.

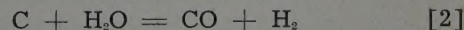
## Bosh Gas Equations

Subject to some alteration by the amount of moisture in the blast and by direct reduction, the gas leaving the combustion zones of a blast furnace has a definite composition. Because a relatively small amount of oxygen is acquired from the charge in the bosh and in the crucible, the products of combustion undergo little change until they enter the shaft. Bosh gas is, therefore, essentially the products of combustion of carbon in a deep fuel bed with air. The relative weights and volumes of reacting materials are expressed by the equation:



$$\left( \text{air} = \frac{79\% N_2}{21\% O_2} = 3.76 \right)$$

Starting with a known mass of C consumed largely by air, Eq 1, but partly by water vapor, Eq 2, the volume and



composition of the bosh gas can be calculated and subsequent changes followed as reactions take place at various elevations in the furnace. As shown in

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Fig. 1, bosh gas is converted to intermediate gas which in turn is converted to top gas.

## Changes in Composition of Gas Stream

The reactions that produce the major changes in the gas stream are given in Fig. 2 in terms of pound mols,\* a convenient unit of volume as well as of mass. Except for the amount of carbon burned at

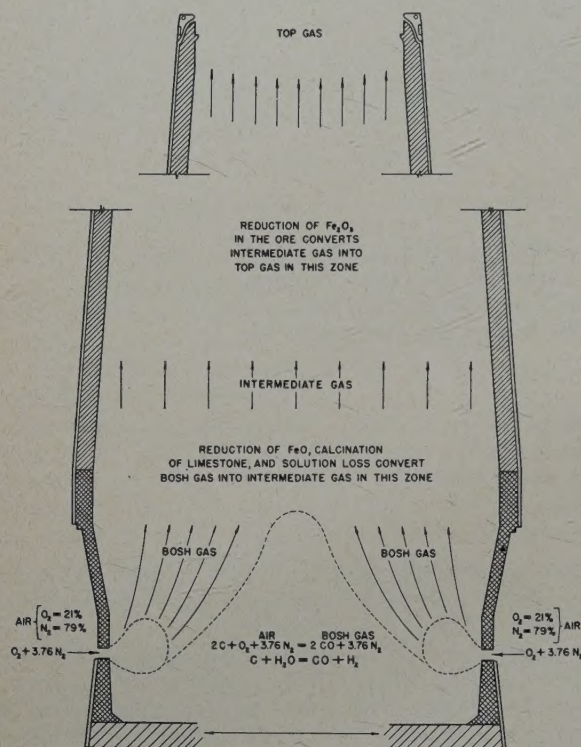


Fig. 1—Major changes in composition of blast furnace gas.

the tuyeres the items reported in Table I are available from routine operating data. A method of calculating the pounds of carbon consumed at the tuyeres has been published.<sup>1</sup>

In setting up the equations and the material balance presented in Fig. 2, it has been assumed that 1086 lb or 90.5 mols of C are gasified at the tuyeres with the moist blast and that 208 lb or 17.33 mols are gasified above the tuyeres with oxygen from the charge. Once the carbon consumed at the tuyeres is fixed, the volume of air required is fixed. In this case, 209.44 lb mols or 79,500 ft<sup>3</sup> of dry air is needed to consume 88 mols of carbon. (379.4 ft<sup>3</sup>/lb mol  $\times$  209.44 lb mols = 79,500 ft<sup>3</sup>).

With a moisture content of about 4 grains per ft<sup>3</sup>, this volume of air will contain 2.5 mols of water which will consume 2.5 mols, or 30 lb, of carbon.

Subject to slight modification by the amount of moisture in the blast and by the CO produced by direct reduction or solution loss in the crucible, the composition of the gas leaving the combustion zones will conform rather closely to that given under bosh gas in Fig. 2. The total volume of gas issuing from

the combustion zones per ton of iron produced will vary with the carbon gasified at the tuyeres. In this case 98,000 ft<sup>3</sup> of gas containing 35 pct CO, 64 pct N<sub>2</sub>, and 1 pct H<sub>2</sub> are formed per ton of iron. At the inward extremities of the combustion zones and particularly in the central idle core where gas flow is restricted, the CO may be higher and the N<sub>2</sub> lower than given in Fig. 2.

A relatively small amount of CO, 2.5 mols or 950 ft<sup>3</sup>, is formed during the reduction of MnO, SiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> in the bosh and in the crucible. There is no way of knowing what proportion of the metalloids is reduced in the hearth. For simplicity, it is assumed that most of the CO from direct reduction enters the gas stream in the bosh.

## Change from Bosh Gas to Intermediate Gas

The term bosh gas refers to the gas formed in the high-temperature combustion zones adjacent to the tuyeres. Because a comparatively small amount of oxygen is removed from the charge in the bosh, the gas stream undergoes little change in this part of the furnace. Near the top of the bosh and in the lower part of the shaft a number of reactions take place because all of them proceed at temperatures ranging from 1100°C down to 800°C. Ferrous oxide is reduced, the limestone calcines, and CO<sub>2</sub>, either from calcination or from indirect reduction, reacts with carbon according to the solution loss reaction. These reactions representing the acquisition of oxygen from the charge as CO and CO<sub>2</sub> are summarized in Fig. 2.

As indicated in Table I, a net ton of pig iron will contain about 1840 lb of Fe equivalent to 2374 lb or 33.05 mols of FeO. It is arbitrarily assumed that one half the H<sub>2</sub> from the combustion zone reacts with 1.25 mols of FeO, and that the remaining 31.80 mols of FeO are reduced with CO. The amount of H<sub>2</sub> involved in reduction is normally relatively small but

Table I. Typical Data for Calculating Changes in Composition of Blast Furnace Gas

| Carbon Balance                                                                       |   | Lb                                                  | Lb Mols |
|--------------------------------------------------------------------------------------|---|-----------------------------------------------------|---------|
| Coke per ton of pig                                                                  |   | 1,560                                               |         |
| Carbon per ton of pig                                                                |   | 1,404                                               | 117.0   |
| Carbon burned with O <sub>2</sub> at tuyeres                                         |   | 1,056                                               | 88.0    |
| Carbon consumed with H <sub>2</sub> O at tuyeres                                     |   | 30                                                  | 2.5     |
| Total carbon at tuyeres                                                              |   | 1,086                                               | 90.5    |
| Carbon dissolved in pig                                                              |   | 80                                                  | 6.66    |
| Carbon used in reducing P <sub>2</sub> O <sub>5</sub> , and MnO and SiO <sub>2</sub> |   | 30                                                  | 2.50    |
| Carbon from coke gasified in furnace                                                 |   | 1,324                                               | 110.33  |
| Carbon from coke gasified at tuyeres                                                 |   | 1,086                                               | 90.50   |
| Carbon from coke gasified above tuyeres                                              |   | 238                                                 | 19.83   |
| Carbon gasified in direct reduction                                                  |   | 30                                                  | 2.50    |
| Carbon gasified in solution loss                                                     |   | 208                                                 | 17.33   |
| Carbon dioxide from limestone                                                        |   | 352                                                 | 8.0     |
| Lb of Fe, FeO, and Fe <sub>2</sub> O <sub>3</sub>                                    |   |                                                     |         |
| 2,000 lb $\times$ 0.92                                                               | = | 1,840 lb Fe per ton pig                             |         |
| 1,840 $\times$ 1.29                                                                  | = | 2,374 lb FeO per ton pig                            |         |
| 2,374                                                                                | = | 33.05 lb mols of FeO                                |         |
| 71.84                                                                                |   |                                                     |         |
| 1,840 $\times$ 1.43                                                                  | = | 2,631 lb Fe <sub>2</sub> O <sub>3</sub> per ton pig |         |
| 2,631                                                                                | = | 16.53 lb mols Fe <sub>2</sub> O <sub>3</sub>        |         |
| 159.68                                                                               |   |                                                     |         |

additions of steam to the blast could lead to a substantial reduction in the amount of CO<sub>2</sub> formed and in the ratio of the carbon gases.

By making appropriate adjustments for the carbon gasified in the reduction of metalloids, and for the carbon dissolved in the iron, it is possible to determine the weight of carbon gasified above the

\* A pound mol or molecular weight of any gas expressed in pounds occupies 359 ft<sup>3</sup> at 32°F and 29.92 in. of Hg or 379.4 ft<sup>3</sup> at 60°F and 14.7 psi.

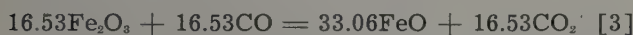


tuyeres. The exact mechanism of gasification is not known, but it seems more logical to assume that gas-solid reactions are more likely to occur than those between two solids such as FeO and carbon. The effect of variations in the amount of C gasified above the tuyeres on the CO/CO<sub>2</sub> ratio will be considered later. For the immediate purpose of illustrating the method, it has been assumed that 208 lb or 17.33 mols of C reacts with CO<sub>2</sub>, a portion of which may be produced by the calcination of 8 mols or 800 lb of calcium carbonate.

By combining the results of the CO and CO<sub>2</sub> balances of Fig. 2, it is noted that the conversion of bosh gas to intermediate gas adds 5.36 mols of CO and 22.47 mols of CO<sub>2</sub> to the bosh gas. This increase of 27.83 mols, equivalent to 10,610 ft<sup>3</sup>, has diluted the N<sub>2</sub> from 64.0 to 58.0 pct. The percentage of CO in the intermediate gas is almost as high as in the bosh gas; 33.4 compared with 35. Due largely to the solution loss reaction, the gas contains but 7.8 pct CO<sub>2</sub> giving a CO/CO<sub>2</sub> ratio of 4.3. Thus if certain assumptions are made, some interesting observations may be made on the changes in the gas stream.

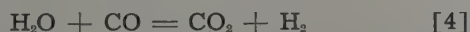
### Conversion of Intermediate Gas to Top Gas

The early step of reduction or the conversion of Fe<sub>2</sub>O<sub>3</sub> through Fe<sub>3</sub>O<sub>4</sub> to FeO takes place at much lower temperatures than the last step of reduction, i.e., the conversion of FeO to metallic iron. It seems permissible, therefore, to think of another major change in composition of the gas stream brought about by the reduction of Fe<sub>2</sub>O<sub>3</sub> to FeO in the upper part of the shaft by the reaction



The effect of this reaction, which involves no increase in volume but merely a conversion of CO to CO<sub>2</sub>, is readily determined as shown in Fig. 2.

The H<sub>2</sub> in the calculated top gas of Fig. 2 is low because the reaction



has not been considered. Some moisture from the charge is decomposed in the upper part of the furnace, but the reactions involved have not been established. Reaction 4 would reduce the CO/CO<sub>2</sub> ratio of 2.03 given for the top gas in Fig. 2 to 1.75 if 4 mols of hydrogen were so formed. The decomposition of water vapor by metallic iron would not alter this ratio. Until more information is available, the ratio given in Fig. 2 is tentative.

Knowing the blast moisture and the carbon used in solution loss and the composition of the top gas, one could determine the amount of H<sub>2</sub> formed in the upper part of the furnace. A comparison of actual CO/CO<sub>2</sub> ratios with calculated ratios based upon the formation of this H<sub>2</sub> by reaction 4 would shed some light on the mechanism of water decomposition in the upper shaft. Moisture added to the skip may react differently from water combined in the ore because the latter would come off at somewhat higher temperature. It is unlikely that moisture in the charge would persist low enough in the furnace in any case to change the intermediate gas.

### Solution Loss and Direct Reduction

Although the writer prefers to think of the gasification of C above the tuyeres as a gas-solid reaction, many prefer to associate this phenomena with the direct reduction of FeO by the reaction



A few calculations will show that the final results are stoichiometrically the same whether we consider the carbon is gasified by reacting with CO<sub>2</sub> gas or with solid FeO. Beginning with the same volume and composition of bosh gas as given in Fig. 2 and

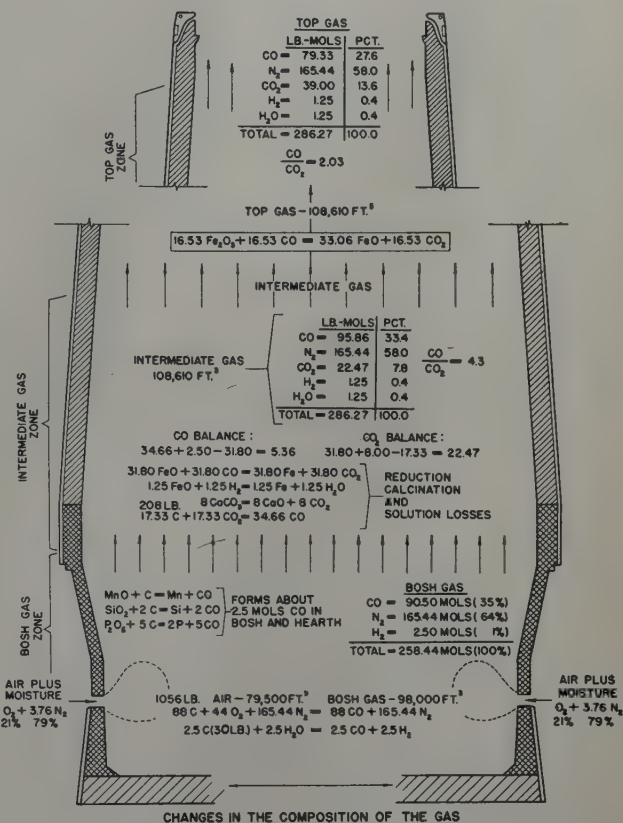
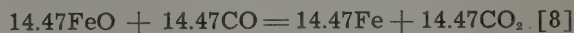
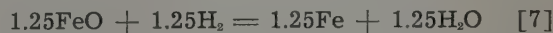
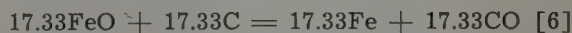


Fig. 2—Detailed changes in composition of blast furnace gas.

considering the effect of gasifying 208 lb of C in direct reduction rather than with solution loss, the reactions for the conversion of bosh gas to intermediate gas are as follows:



The net result of these three reactions is a gain of 2.86 mols of CO and a gain of 14.47 mols of CO<sub>2</sub>. If 2.5 mols of CO from direct reduction is added, as was done in the CO balance of Fig. 2, the same total increase of 5.36 mols of CO is obtained. For CO<sub>2</sub> the gain is also the same as in Fig. 2, if 8 mols from the limestone is added. According to this mechanism, the conclusion would be that 17.33 mols of FeO out of 33.05, or about 56 pct of the iron, is reduced directly with solid C and 44 pct with H<sub>2</sub> and CO. To the writer the implications of such a division of reduction is not as meaningful as the statement that 208 lb of C are gasified with CO<sub>2</sub> with a loss of 5,830 Btu per lb of C. However, the method described can be used to study the process regardless of the preferred mechanism for reduction.



The gasification of carbon by oxygen from the charge is presumably more detrimental if it occurs at lower levels in the furnace. Unfortunately top-gas analyses or the calculations under discussion do not show where solution loss or direct reduction occur. They merely show the amount of C involved, the thermal effect and the effect on the volume and composition of the gas stream. Obviously carbon deposition cannot be isolated by the use of top-gas analyses.

### Solution Loss and Reducing Power of Gas Stream

The amount of C consumed at the tuyeres to satisfy the heat requirements, the amount of  $\text{CO}_2$  from the limestone, and the moisture in the blast all have a bearing upon the  $\text{CO}/\text{CO}_2$  ratio in the region of the mantle. Solution loss has a very pronounced effect upon this ratio because it involves the conversion of 1 mol of  $\text{CO}_2$  into 2 mols of CO. By calculations similar to those in Fig. 2 the effect of each of these factors can be studied.

Intermediate gas compositions were calculated for amounts of solution loss ranging from 0 to 300 lb and for amounts of carbon consumed at the tuyeres

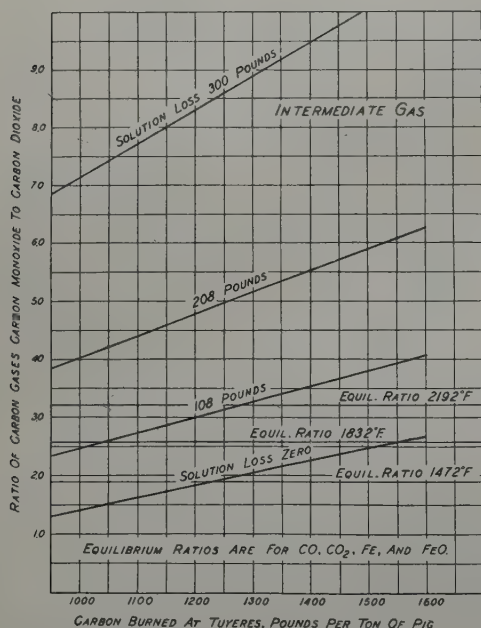


Fig. 3—Equilibrium and calculated carbon gas ratios in the intermediate gas.

ranging from 1000 to 1600 lb. This range of carbon burned at the tuyeres would be equivalent to from 1400 to 2300 lb of coke charged per ton of iron. In making these calculations the volume of  $\text{CO}_2$  from the flux and the effect of moisture in the blast were held constant. The results of these calculations showing the effect of carbon burned at the tuyeres and solution loss on the  $\text{CO}/\text{CO}_2$  ratio in the intermediate gas are shown as generalized curves in Fig. 3. Equilibrium ratios of the carbon gases in contact with  $\text{FeO}$  at temperatures of 1472°, 1832°, and 2192°F have also been plotted in this figure to show the conditions under which these ratios are exceeded and reduction can occur. Equilibrium ratios for other temperatures, taken from Austin and Day,<sup>2</sup> are given in Table II.

It seems evident from Fig. 3 that when the solution loss exceeds 208 lb, the intermediate gas will be reducing towards ferrous oxide. Consider, for example, the case when 1200 lb of C is consumed at the tuyeres. The consumption of 208 lb of C by solution loss, 30 lb by reduction of metalloids, and 80 lb by solution in the iron, would mean that 1518 lb of C or about 1700 lb of coke are charged per ton

Table II. Equilibrium Ratios of Carbon Gases in Contact with  $\text{FeO}$

| Temperature |       | Ratio<br>$\text{CO}/\text{CO}_2$ | Temperature |       | Ratio<br>$\text{CO}/\text{CO}_2$ |
|-------------|-------|----------------------------------|-------------|-------|----------------------------------|
| Deg F       | Deg C |                                  | Deg F       | Deg C |                                  |
| 752         | 400   | 0.74                             | 1,652       | 900   | 2.24                             |
| 932         | 500   | 0.96                             | 1,832       | 1,000 | 2.57                             |
| 1,112       | 600   | 1.17                             | 2,012       | 1,100 | 2.88                             |
| 1,292       | 700   | 1.53                             | 2,192       | 1,200 | 3.21                             |
| 1,472       | 800   | 1.90                             | 2,372       | 1,300 | 3.47                             |

of iron. Under these conditions, the  $\text{CO}/\text{CO}_2$  ratio of the intermediate gas is equal to 4.75 compared with an equilibrium ratio of 1.9 at 1472°F (800°C).

For an overall appraisal of the situation it appears that a  $\text{CO}/\text{CO}_2$  ratio of 3 or higher should be maintained. Such a ratio would require that a minimum of 1200 lb of C be burned at the tuyeres if 108 lb of C be consumed in solution loss, see Fig. 3. Gruner's ideal furnace would require the consumption of over 1700 lb of C at the tuyeres, equivalent to over 2000 lb of coke charged, to obtain a  $\text{CO}/\text{CO}_2$  ratio of 3 in the intermediate gas. Thus it may be seen that only when large amounts of fuel are needed to satisfy fuel requirements can furnaces operate without solution loss. It appears that a solution loss of some 200 lb, which is typical of Lake ore practice, may be reduced to about 100 lb without exhausting the reducing power of the intermediate gas. The combustion of an additional 100 lb of C at the tuyeres rather than the gasification of an equal amount above the tuyeres would increase the heat made available to the process by about 1,000,000 Btu. The fact that about 200 lb of C is consumed above the tuyeres merely means that operations are not on properly sized and easily reduced ore burdens.

Assuming that 108 lb, or 9 mols, of C must be gasified above the tuyeres to maintain the reducing power of the gas, it follows that 9 mols of  $\text{FeO}$  must be reduced directly with solid carbon. This would correspond with about 27 pct of the 33.05 mols of  $\text{FeO}$  needed to produce the metallic iron in a net ton of pig iron. For those who prefer to think in terms of the solid carbon or direct reduction reaction, it appears, therefore, that some 25 pct of direct reduction is necessary in typical Lake ore practice to maintain the reducing power of the bosh gas.

### Effect of Countercurrent Flow

Under the conditions of countercurrent flow of the blast furnace, the descending ore burden comes in contact with ascending gas progressively higher in CO and progressively hotter. This offers distinct advantages because the charge richest in  $\text{FeO}$  comes in contact with gas at the lowest temperature and with the lowest  $\text{CO}/\text{CO}_2$  ratio. On the other hand, the charge containing very little  $\text{FeO}$  in the final



stages of reduction comes in contact with bosh gas containing little, if any, CO<sub>2</sub>.

Calcination of the limestone and the reaction of CO<sub>2</sub> with C begin very slowly at about 1400° and increase rapidly with temperature above 1800°F. In preparing Fig. 4 it has been assumed for the sake of simplicity that reduction, calcination, and solution loss take place in 10 equal steps as the charge moves through a temperature range of 1400° to 2400°F. As indicated, bosh gas containing no CO<sub>2</sub>

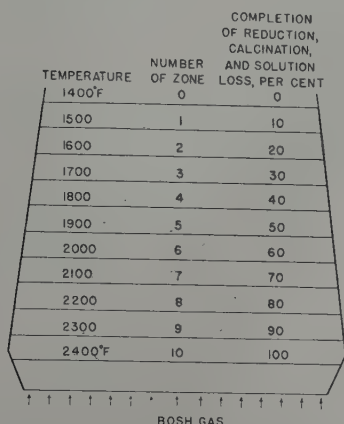


Fig. 4—Steps in the conversion of bosh gas to intermediate gas.

enters zone 10, in which the last 10 pct of FeO is reduced to metallic iron. Moving through the successive zones, the gas stream acquires oxygen from the charge and finally emerges as intermediate gas having acquired the oxygen associated with the first stages of reduction of FeO and the first stages of calcination. As shown in Fig. 3, this gas has a definite composition under fixed conditions of fuel consumption, blast moisture, limestone requirements, and solution loss.

#### Calculated and Equilibrium Ratios of Carbon Gases

As shown in Table II, higher CO/CO<sub>2</sub> ratios must be maintained to facilitate reduction at higher temperatures. For example, the equilibrium ratio increases from 1.9 at 1400°F to 3.5 at 2400°F. Fortunately, the gas is very rich in CO at the highest temperature, as indicated by the calculated CO/CO<sub>2</sub> ratios given in Fig. 5. It appears that the closest approach to equilibrium occurs in the early stages of FeO reduction and in the early stages of calcination. In this cooler part of the shaft the equilibrium ratios are somewhat less than 2 whereas the calculated ratio at the lowest temperature indicates a value of 3 for the CO/CO<sub>2</sub> ratio. When 1200 lb of C are burned at the tuyeres, a solution loss of 108 lb will, it appears, maintain reducing conditions in the gas stream. If conditions of higher fuel consumption or higher solution loss were assumed, a series of generalized curves similar in shape to the upper one in Fig. 5, but at higher positions, would be obtained.

#### Nitrogen in Top Gas as Key to Solution Loss

In as much as the N<sub>2</sub> of the blast is relatively inert and passes through the furnace without reaction, it can be very useful as a measure of solution loss or direct reduction.

Brief reference to Fig. 2 will show how and to

what extent a change in solution loss alters the volume of the gas and in turn the degree of the dilution of nitrogen. Each pound mol of C that reacts with CO<sub>2</sub>



increases the volume of the gas stream by 1 mol. A mol of CO<sub>2</sub> is consumed, but 2 mols of CO are formed by reaction 9.

If in place of the 208 lb of solution loss, considered in Fig. 2, only 100 lb of C is gasified, the gas volume will be reduced by 9 mols. That is the 286.27 mols of intermediate gas and top gas will be reduced to 277.27 mols. The constant volume of 165.44 mols of N<sub>2</sub> is now equal to 59.7 pct of the total volume; an increase of 1.7 pct over the value of 58.0 pct reported in Fig. 2. Thus, a decrease of 108 lb in solution loss results in an increase of 1.7 pct in the N<sub>2</sub> content of the intermediate and in the top gas. For a fixed coke rate high N<sub>2</sub> means low solution loss.

In a given practice the CO<sub>2</sub> from the stone and the moisture in the blast will remain fairly constant but their effects on N<sub>2</sub> dilution are appreciable. For example, an increase of 200 lb of CaCO<sub>3</sub> or 2 mols would increase the gas volume to 288.27 mols, thus reducing the N<sub>2</sub> from 58.0 to about 57.5 pct. Similarly, each mol of C consumed in the water gas reaction



adds 2 mols of gas without contributing any nitrogen. Thus one additional mol of C consumed at the tuyeres with moisture in the blast and 2 additional mols of CaCO<sub>3</sub> in the limestone dilute the N<sub>2</sub> to about

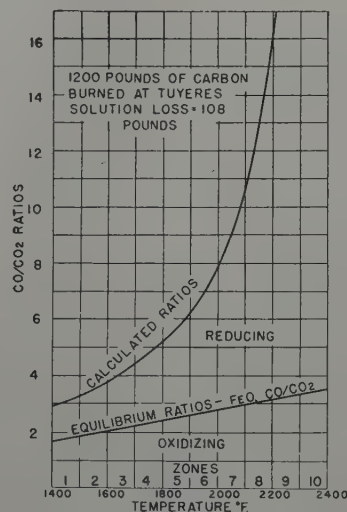


Fig. 5—Calculated and equilibrium carbon gas ratios at various temperatures.

the same degree. The specific affects of solution loss, CO<sub>2</sub> from the stone and moisture in the blast will be considered in greater detail later.

Fuel consumption also has a bearing upon the dilution of nitrogen. High fuel requirements normally mean more air and more N<sub>2</sub> per ton of pig. The combined action of solution loss, calcination, and direct reduction in diluting the N<sub>2</sub> will generally be less when the fuel consumption is high. In other words, a high N<sub>2</sub> content of the top gas is normally



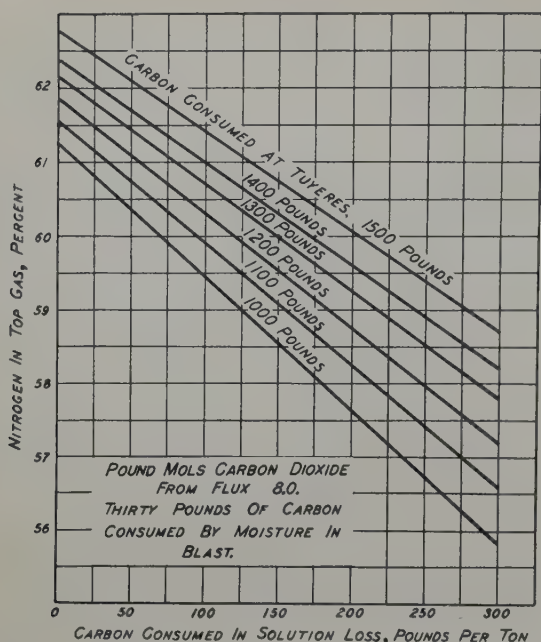


Fig. 6—Fuel consumption solution loss and the nitrogen content of top gas.

associated with high fuel consumption. Sufficient progress has been made in equipment to get continuous records of top-gas composition to warrant further study of the significance of such data as an index of furnace reactions.

A generalized picture of the effect of solution loss upon the  $N_2$  content of the top gas is given in Fig. 6. Following the methods previously described, the composition of the top gas was calculated for zero up to 300 lb of solution loss and for 1000 to 1500 lb of C at the tuyeres per ton of pig iron. If the fuel consumption is high, the nitrogen in the blast required to consume this large amount of carbon suffers less dilution by  $CO_2$  from the limestone, by the solution loss reaction and by the direct reduction of metalloids. With a constant solution loss of 200 lb

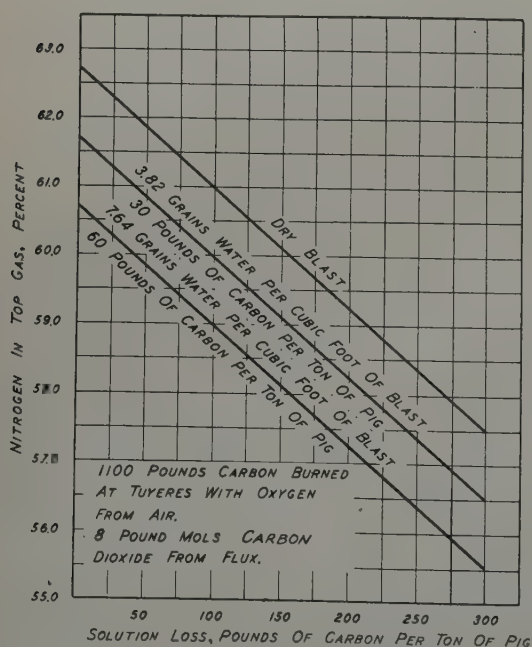


Fig. 7—Moisture in the blast and nitrogen in the top gas.

the top gas will, according to Fig. 6, contain about 60 and 57.6 pct  $N_2$ , respectively, when 1500 and 1000 lb of C are burned at the tuyeres.

When fuel requirements are fairly fixed as indicated by each of the six curves, the  $N_2$  in the top gas becomes an index of solution loss. For example if the heat requirements are such as to demand about 1100 lb of C at the tuyeres, the  $N_2$  in the top gas will drop from 59.9 to 58.2 pct if the solution loss increases from 100 to 200 lb per ton of iron. Such changes in  $N_2$  are readily detected so that with properly prepared curves to compensate for moisture in the blast and  $CO_2$  from the stone, top-gas analyses afford a direct means of following solution loss.

In order to observe the dilution of  $N_2$  in the top gas by blast moisture, calculations were made for three levels of moisture in the blast; dry blast, 3.82 and 7.64 grains-ft<sup>3</sup>. With these respective amounts of moisture in the blast, zero, 30 and 60 lb of C would be consumed per ton of iron. This assumes a constant volume of 82,500 ft<sup>3</sup> of dry air, capable of burning 1100 lb of C at the tuyeres per ton of iron

$$\left( \frac{4.76 \times 379.4}{24} = 75 \text{ ft}^3 \text{ air per lb of C} \right).$$

The action of moisture in the blast as a  $N_2$  diluent is summarized in Fig. 7 for a wide range of solution loss. An increase of 3.82 grains of blast moisture lowers the  $N_2$  in the top gas by about 1 pct. It does so of course because this amount of moisture will consume 2.5 mols of C and produce 5 mols or 1897 cu ft of  $H_2$  plus  $CO$ .

Except for the endothermic effect of the water gas reaction it represents a form of oxygen enrichment. A pound mol of water vapor will gasify a pound mol of C whereas it requires 2.38 mols of air per mol of C, see Fig. 1. Thus the combustion potential of 1 ft<sup>3</sup> of water vapor is equivalent to 2.38 ft<sup>3</sup> of dry air. On the gas produced side, it is of interest to note that 2 mols of  $H_2$  plus  $CO$  are produced per mol of C consumed with  $H_2O$  whereas 2.88 mols of  $CO$  and  $N_2$  are produced per mol of C gasified with dry air. In other words, high moisture favors a more rapid rate of driving because of the greater combustion potential of moisture and also because less gas is produced per pound of C gasified.

### Effect of Limestone on Nitrogen in Top Gas

The effect of  $CO_2$  from the stone as shown in Fig. 8 can be seen very readily if it is remembered that each additional 100 lb of flux represents about 100 lb, or 1 mol, of  $CaCO_3$  equivalent to 1 mol of  $CO_2$ . An increase from 800 to 1100 lb of flux means, therefore, an addition of about 3 mols of  $CO_2$  or roughly 1.0 pct of the 286.27 mols shown in Fig. 2. Since the gas contains about 58.0 pct  $N_2$  such a percentage reduction would be a reduction of about 0.6 pct  $N_2$ . Such a reduction in  $N_2$  can be observed for each of the three levels of carbon consumption in Fig. 8. In general, the effects of changes in the amount of flux used will be masked by the effect of solution loss or blast moisture. However, adjustments must be made for variations in the flux to isolate the effect of solution loss.

Since the details of calculations for dealing with furnace problems in pound mols have been given in the hope that it may be of value in studying the smelting process, it may be permissible to show how the method assists in following other changes as well as changes in solution loss. Suppose, for example,



that 900 lb of high-combined moisture material were substituted for 900 of a low-combined moisture material such as sinter. An increase of 10 pct in combined moisture would represent 90 lb, or 5 mols, of water vapor. This would be equivalent to an increase of about 1.75 pct in the volume of the gas liberated in the upper part of the shaft and may necessitate a slower rate of operation in the case of a furnace already blown near the maximum rate.

### Solution Loss and Volume of Gas Generated

Since 1938, the demand for steel and pig iron has been conducive to operation of blast furnaces at maximum rates consistent with efficiency and the production of flue dust. Under these conditions, the linear velocity of the gas through the stock imposes the final limitation on the amount of wind that can be blown in a given furnace. Although solution loss or the oxidation of carbon above the tuyeres by oxygen in the charge reduces the volume of gas generated per pound of carbon gasified in the furnace as a whole, the use of high-top pressure, described in a number of reports,<sup>3-5</sup> is a more effective

transfer. It is conceivable, therefore, that a decrease in solution loss may result in a temporary loss of tonnage. Actually, a decrease of 108 lb of solution loss would increase the heat available to the process by about 1,000,000 Btu. It seems more likely that such an increase in available heat would result in some increase in hearth temperature which would in turn permit a reduction in fuel, in air, and in the gas produced to the end that there would be a reduction in fuel required but not in tonnage. A high-solution loss of carbon does not appear to be a proper way to reduce gas velocities in the furnace shaft. Size preparation of the ore or high-top pressures would appear to be more promising methods of reducing the linear velocity of the gas through the stock.

### Summary and Conclusions

Further study of the gas phase of the blast furnace process offers a means of learning more about the process. Simple calculations based upon the use of the pound mol to make a material balance indicate that the consumption of about 100 lb of C in solution loss or by direct reduction of FeO will maintain a reducing gas in the region of the mantle in typical Lake ore practice. Few data are available but it appears that about 200 lb of C normally is consumed above the tuyeres. More reducible burdens and burdens better prepared physically will be necessary to make an additional million Btu available to the process by a reduction of 100 lb in the C gasified above the tuyeres.

An increase in solution loss temporarily increases the rate of furnace driving for a constant rate of blowing merely because more carbon is gasified with oxygen from the charge. However, since the heat available is reduced, more fuel eventually must be used so that in the end solution loss in excess of about 100 lb means a loss of both tonnage and efficiency. With better prepared burdens physically or with higher top pressures, the additional gas produced by burning more carbon at the tuyeres should not present a problem.

The generalized curves illustrate what can be done with calculations similar to those outlined in the paper. They are not intended for general use but as a guide for similar curves made to fit a particular practice. It is to be hoped that continuous top-gas analysis will be used in interpreting what is going on in the furnace to the end that more will be learned about the basic features of the smelting process. All will agree that a better understanding of the process is needed to appraise the value of new raw materials as well as innovations in practice such as high-top pressures, beneficiated ore burdens, and oxygen enriched blast.

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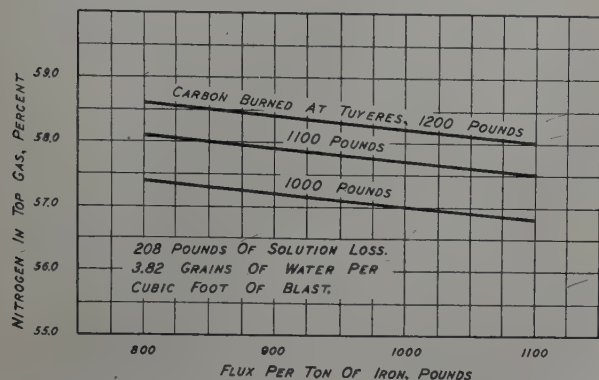


Fig. 8—Flux requirements and nitrogen in the top gas.

way of reducing linear gas velocities without disturbing the thermal balance of the operation.

In the calculations of Fig. 2, 208 lb of C are consumed above the tuyeres and 1056 at the tuyeres with dry air. It may be assumed that a more easily reduced burden, better gas distribution, and smaller limestone reduce solution loss by 108 lb, or 9 mols, of C. Under these conditions the 9 additional mols of C to be consumed at the tuyeres per ton of pig iron would require 21.42 additional mols of air and 25.92 additional mols of bosh gas would be produced per ton of pig iron.

$$\left( 9 \times \frac{4.76}{2} = 21.42; 9 \times \frac{5.76}{2} = 25.92 \right)$$

This may be compared with the combustion reaction, Fig. 1. This increase in the volume of bosh gas would be partly offset by a reduction of 9 mols in the gas produced by solution loss.

The net effect of more bosh gas and a reduction in the volume of CO from solution loss would be the addition of 16.92 mols of intermediate gas per ton of pig. On the basis of 286.27 mols of intermediate gas, this is equivalent to an increase of 5.9 pct in the volume of the gas per ton of iron.

Such an increase in the gas to be forced through the charge may, in the case of a furnace operating near critical gas velocities, lead to channelling, an increase in dust production, and less favorable heat



# Metallographic Study of the Martensite Transformation in Lithium

by J. S. Bowles

THE martensite transformation in lithium, discovered by Barrett,<sup>1</sup> has been studied extensively by X-ray techniques by Barrett and Trautz,<sup>2</sup> and Barrett and Clifton.<sup>3</sup> The present paper reports the results of an investigation into the metallographic characteristics of lithium martensite. Such an investigation has not been carried out before.

The spontaneous transformation in lithium consists of a change from a body-centered cubic to a close-packed hexagonal structure with the hexagonal layers in imperfect stacking sequence.<sup>4</sup> As far as is known at present, this transformation can be regarded as being crystallographically equivalent to the body-centered cubic to close-packed hexagonal transformation that occurs in zirconium,<sup>5</sup> although stacking errors have not been reported in zirconium.

From a study of the orientation relationships in zirconium, Burgers<sup>5</sup> has proposed that the martensite transformation, b.c.c. to c.p.h., occurs by a heterogeneous shear on the system (112)  $[11\bar{1}]$ . The crystallographic principle underlying this proposal is that the configuration of atoms in the (112) plane of a b.c.c. structure is exactly the same as that in the (10 $\bar{1}0$ ) plane of a close-packed hexagonal structure based on the same atomic radius. The pattern in

both these planes is a rectangle  $d \times \frac{2\sqrt{2}}{\sqrt{3}} d$  where

$d$  is the atomic diameter. Thus a close-packed hexagonal structure can be built up from a body-centered cubic structure by displacing the (112) planes relative to each other.\* This mechanism leads to orientations that can be described by the relations:

$$(110)_{b.c.c.} // (0001)_{c.p.h.}; [\bar{1}11]_{b.c.c.} // [11\bar{2}0]_{c.p.h.}$$

Observations confirm these relations. In zirconium, Burgers' measurements indicated an angle of 0° to 2° between the close-packed directions, while Barrett's measurements on lithium indicated an angle of 3°.

According to the Burgers' mechanism, the martensite habit plane for this transformation would be expected to be the (112)<sub>b.c.c.</sub> plane, for this plane would not be distorted by the transformation. One of the purposes of this investigation was to find out whether the observed lithium habit plane agrees with this prediction of the Burgers' mechanism.

## Experimental Procedure

**Materials:** The lithium was from the same purified ingot used by Barrett and Trautz.<sup>2</sup> The Bridgman technique was used to produce single crystals. To maintain a temperature gradient in the melt, during the production of these crystals, it was necessary to use a steel mould with a wall thickness of only 0.015 in.

**Metallographic Techniques:** Lithium specimens could be given an excellent metallographic polish by swabbing them gently with cold methyl or ethyl alcohol.† The best results were obtained with methyl alcohol saturated with the reaction product, lithium alcoholate. With higher alcohols the reaction became progressively slower and the attack became an etch pit attack rather than a polish attack. Butyl and amyl alcohols were used for macroetching.

After polishing, it was necessary to remove all traces of alcohol from the specimens; otherwise, on subsequent quenching in liquid nitrogen, the alcohol froze to a glassy film. The alcohol was removed with dry benzene. The benzene in turn had to be removed before quenching, but since it does not react with lithium it could be allowed to evaporate. The specimens could then be quickly quenched before they began to tarnish. This operation could be carried out in air on all but excessively humid days when it was advisable to use an atmosphere of dry nitrogen or argon. For examinations at room temperature, the specimens could be transferred directly from the benzene bath into a bath of mineral oil. In mineral oil the specimens oxidized slowly by the diffusion of oxygen through the oil but the structure remained visible for about an hour.

**Lithium Martensite:** Specimens prepared in the manner described above transformed spontaneously to martensite with an audible click when quenched into liquid nitrogen; i.e.,  $M_s$  was above the boiling point of nitrogen (77°K). The disparity between this result and the  $M_s$  temperature of 71°K, found by Barrett and Trautz, is probably to be attributed to the large grain size and freedom from mechanical deformation of the specimens used in the present work.

The relief effects produced by the transformation did not disappear when specimens were quenched from liquid nitrogen into mineral oil at room temperature. This permitted the microstructures to be studied at room temperature where, of course, the martensitic phase was no longer present. Typical micrographs of lithium "martensite" made at room temperature are reproduced in figs. 1, 2, and 3. As anticipated by Barrett and Trautz, the microstruc-

\* It should be noted that the array on the (110)<sub>b.c.c.</sub> plane cannot be converted into an exact hexagonal array by the simple shear proposed by Burgers, since the spacings of the (112)<sub>b.c.c.</sub> and (10 $\bar{1}0$ )<sub>c.p.h.</sub> planes are not exactly equal. A contraction would have to be superimposed on the proposed shear.

† Sodium can also be polished metallographically in this way, using propyl alcohol instead of methyl alcohol.

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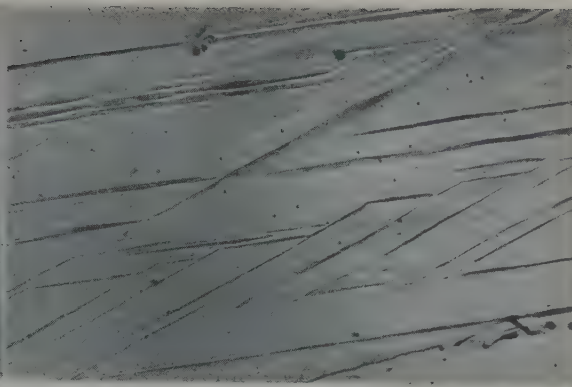


Fig. 1 (upper left)—Lithium martensite relief effects photographed at room temperature. X100.

Fig. 2 (upper right)—Lithium martensite relief effects photographed at room temperature. X150.

Fig. 3 (lower left)—Lithium martensite relief effects photographed at room temperature. X200.

tural characteristics of lithium martensite were essentially similar to those of other martensitic phases. The relief effects produced by the transformation consisted essentially of a simple tilting of the surface about its intersection with the habit plane. This type of relief appeared to be typical of martensite transformations. The lithium martensite plates also frequently showed a set of transverse markings. As in other systems, the transformation at  $M_s$  appeared to be a highly cooperative affair, for a whole network of plates suddenly appeared. Apparently many plates, both in the same crystal and in neighboring crystals, were triggered off by the formation of the first plate. The zig-zag linkage, which is so predominant a feature of other martensitic structures, also occurred very frequently.

When a specimen was covered with a frozen film of alcohol, martensite relief effects were not produced on the surface on quenching into liquid nitrogen, i.e., these films appeared to suppress the transformation. These films were quite transparent, and although they had the form of a cracked mosaic, the microstructure of the underlying lithium could be seen quite clearly. Many specimens coated with alcohol films were cooled to the melting point of nitrogen ( $63^\circ\text{K}$ ), i.e., more than  $14^\circ$  below  $M_s$  and no relief effects were ever observed. Films of frozen propane caused the same behavior. X-ray diffraction experiments were carried out at liquid nitrogen temperature to see whether the films completely inhibited transformation. In general diffraction lines of the martensite phase were detected in these specimens. There appear to be two possible interpretations of these results. The films may have inhibited transformation at the surface but not in the interior, or the films may not have been continuous on the backs and edges of the specimen that could not be polished properly, and transformation may have occurred there.

**The Habit Plane:** The persistence of the relief effects on quenching from liquid nitrogen into mineral oil at room temperature greatly facilitated the determination of the lithium habit plane, for it meant

that trace measurements could be made at room temperature. Orientations were determined by the back-reflection method using a precision camera designed to permit Laue patterns to be taken at previously selected positions on the specimen. To prevent the diffraction pattern of the base from appearing in the photograph, a plug of litharge-glycerin cement was inserted in the aluminum specimen holder. Crystals that passed completely through the specimen were selected to prevent the Laue patterns of underlying crystals, as well as of the crystal under investigation, from appearing on the film.

The method of determining the habit plane from the observed traces consisted of plotting the zone that was normal to each trace in a single stereographic triangle and determining the common point of intersection of all the zones. In this way an unambiguous solution for the habit plane could be obtained without making measurements of the traces of any single plate on more than one surface. The procedure is illustrated in fig. 4. Fourteen trace normals in four different crystals all passed within  $\pm 1\frac{1}{2}^\circ$  of the solution indicated in fig. 4. This plane, which is  $10\frac{1}{2}^\circ$  from (110) can be described approximately by the indexes  $\{441\}_{h.c.c.}$ .

### Discussion of Results

The result obtained for the lithium habit plane is of interest for several reasons. First, it is now clear that the observed habit plane is not that predicted by the Burgers' mechanism and that this mechanism will therefore have to be revised. Second, the observed habit plane is closely similar to the habit

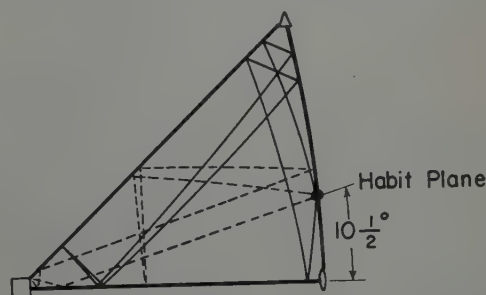


Fig. 4—Stereographic projection of the pole of the lithium martensite habit plane illustrating the method of determining the habit plane from trace measurements on single surfaces.



planes utilized in a number of other martensite transformations in body-centered cubic metals (table I). It seems reasonable to conclude from this recurrence of nearly the same habit plane for essentially equivalent transformations in quite different systems, that the choice of habit plane is determined by the geometry of the transformation mechanism rather than by other considerations.

The relief effects produced by the transformation consisted essentially of a simple tilting of the surface about its intersection with the habit plane. This means that the transformation involves a homogeneous distortion of the original structure, in which the habit plane is a plane of zero distortion. However, since the body-centered cubic structure is a space lattice with a single atom motif, it will remain

**Table I. Habit Planes in Martensite Transformations**

| System | Transformation                                                  | Habit Plane |
|--------|-----------------------------------------------------------------|-------------|
| Cu-Al  | b.c.c. $\rightarrow$ Distorted c.p.h. ( $\beta'$ ) <sup>9</sup> | (441)       |
| Cu-Al  | b.c.c. $\rightarrow$ c.p.h. ( $\gamma'$ ) <sup>9</sup>          | (221)       |
| Cu-Zn  | b.c.c. $\rightarrow$ f.c.t. (?) <sup>10</sup>                   | (551)       |
| Cu-Sn  | b.c.c. $\rightarrow$ Structure unknown <sup>10</sup>            | (331)       |
| Au-Cd  | b.c.c. $\rightarrow$ Orthorhombic <sup>11</sup>                 | (331)       |
| Li     | b.c.c. $\rightarrow$ c.p.h.                                     | (441)       |

a space lattice with a single atom motif throughout any succession of homogeneous distortions. Clearly then, the observed change in structure cannot be achieved by the observed homogeneous distortion. Additional atom movements that do not cause any observable change in shape of the plate must also occur. The transformation b.c.c.  $\rightarrow$  c.p.h. therefore involves two distortions of the original lattice, one homogeneous and the other heterogeneous. In this respect it is analogous to the f.c.c.  $\rightarrow$  b.c.t. transformation that occurs in Fe-C alloys<sup>6</sup> and the f.c.c.  $\rightarrow$  f.c.t. transformation that occurs in In-Tl alloys.<sup>7</sup>

Recent studies of these transformations have demonstrated clearly the nature of the problems involved in the determination of the crystallographic mechanisms of martensite transformations. It is necessary to decide first, what net atom displacements are needed to build up a unit cell of the new phase, and second, how this "unit distortion" is repeated throughout the parent lattice. The criterion of an acceptable mechanism is, of course, that it be consistent with all the geometrical features of the transformation, e.g., orientation relationships, habit plane, etc.

In the Fe-C and In-Tl transformations, the net atom displacements that occur are those that lead to the smallest overall distortion of the parent lattice. That this is also true for at least one of the b.c.c.  $\rightarrow$  c.p.h. transformations is indicated by the work of Kurdjumow and Miretsky<sup>8</sup> who have shown that the assumption of minimum overall distortion leads to a prediction of the observed superlattice in Cu-Al martensite. Since these minimum displacements are exactly those proposed by Burgers, it seems very likely that the Burgers' mechanism is correct as far as the displacements in any small region are concerned.

If this conclusion is correct, then to modify the Burgers' mechanism so that it becomes consistent with the observed habit plane and relief effects necessitates a consideration of the manner in which this unit distortion is repeated throughout the lattice.

In the Fe-C and In-Tl transformations, the unit distortion is not repeated as a simple homogeneous

distortion throughout the lattice. It is necessary to describe the correspondence between atom positions before and after transformation by two distortions, the first homogeneous and the second heterogeneous. The homogeneous component accounts satisfactorily for the observed habit plane and relief effects, and in the indium-thallium alloys for the observed propagation of the transformation distortions at an interface parallel to the habit plane. The heterogeneous component is necessary to complete the transformation, and accounts for the transverse markings that are seen in martensite plates. The problem of explaining the observed habit plane and relief effects in the b.c.c.  $\rightarrow$  c.p.h. transformation probably has an analogous solution, but a geometrical analysis of the distortion indicated by the relief effects will be needed before a complete description of the transformation mechanism can be given. Since lithium is not a suitable material for such work, it will probably be simpler to carry out such an analysis for one of the other systems.

### Summary

1. Techniques have been developed for the metallographic examination of lithium and the microstructural characteristics of lithium martensite are described.

2. The lithium habit plane has been shown to be approximately {441}. This is not in agreement with Burgers' prediction of {112} but is closely similar to the habit planes utilized in other martensite transformations in body-centered cubic metals.

3. The atom movements proposed by Burgers are probably correct for they are consistent with the observed superlattice in Cu-Al martensite. To modify Burgers' mechanism so that it becomes consistent with the observed habit plane and relief effects, it will be necessary to find out how the "Burgers' unit distortion" is repeated throughout the lattice.

### Acknowledgment

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# Plastic Deformation and Diffusionless Phase Changes In Metals — The Gold-Cadmium Beta Phase

by L. C. Chang and T. A. Read

Diffusionless transformation in Au-Cd single crystals containing about 50 atomic pct Cd was investigated by means of X-ray analysis of the orientation relationships, electrical resistivity measurements, and motion picture studies of the movement of boundaries between the new and old phases during transformation. The nucleation of diffusionless transformation by imperfections and the generation of imperfections by diffusionless transformation were discussed.

THAT connections exist between plastic deformation and diffusionless phase changes has long been recognized. Thus it is often possible to produce a diffusionless phase change in a temperature range, above that in which the change occurs spontaneously, by cold-working the initial phase.

Certain aspects of the dislocation theory of the plastic deformation of crystalline solids also provide for a rather direct connection between the processes involved in plastic deformation and in diffusionless phase changes. Heidenreich and Shockley<sup>1</sup> have pointed out that simple edge dislocations in f.c.c. metals are probably unstable, and that the more probable lattice imperfections, called extended edge dislocations, consist of two half dislocations separated by a distance of the order of magnitude of 100Å. The region about two atomic planes thick between the half dislocations because of this stacking fault may be described as having the hexagonal close-packed structure. Presumably the stacking faults observed by Barrett<sup>2</sup> after cold-working f.c.c. Cu-Si alloys resulted from the passage of such half dislocations through the lattice of the initial phase.

It is now becoming clear that the development of a detailed theory of the atomic movements involved in diffusionless phase changes will require a consideration of the role played by lattice imperfections, just as such considerations are necessary to the understanding of plastic deformation mechanisms. This point of view has been recently set forth, for example, by Cohen, Machlin, and Paranjpe<sup>3</sup> who pointed out the role which might be played by screw dislocations in nucleating diffusionless phase changes.

The present paper reports on some aspects of the diffusionless phase change in single crystals of the beta phase alloy Au-Cd which serve to emphasize further the importance of lattice imperfections in diffusionless phase changes.

The diffusionless phase change of Au-Cd possesses

several remarkable features. One of these is that the interface between the high-temperature beta phase and the low-temperature orthorhombic phase typically moves with a low velocity, in contrast to the behavior observed in the transformation of austenite to martensite. Motion pictures of this slow interface motion have been prepared in the course of the work reported here.

Another important feature of the Au-Cd transformation is the small amount of undercooling observed. The reverse transformation occurs on reheating to a temperature only 20° higher than the transformation temperature observed on cooling, and under some circumstances the hysteresis observed is substantially less than this. This narrow temperature range between transformation on heating and cooling is presumably in part a consequence of the fact that the transformation requires a lattice shear of only about 3°.

Finally, the orthorhombic product phase possesses unusual mechanical properties, as was first pointed out by Ölander<sup>4</sup> and Benedicks.<sup>5</sup> After completion of the transformation on cooling the specimen can be severely deformed, yet on the release of load it springs back to its original shape in a rubber-like manner. Explanation of this phenomenon will require an understanding of the lattice imperfections in the orthorhombic structure and, correspondingly, of those in the initial body-centered cubic structure.

Single crystals of Au-Cd alloy containing 47.5 and 49.0 atomic pct Cd were prepared from fine gold (99.95 pct purity) and chemically pure cadmium (99.99 pct purity) by melting the alloy in an evacuated and sealed fused quartz tubing and growing into single-crystal form by the Bridgman method. The Au-Cd alloy containing 47.5 atomic pct Cd undergoes a diffusionless transformation from an ordered body-centered cubic structure to an orthorhombic structure when it is cooled to about 60°C, while the reverse transformation takes place when the alloy is heated to about 80°C, according to electrical resistivity studies. The structures of these two phases have been studied by Ölander,<sup>4</sup> reinvestigated by Bystrom and Almin.<sup>6</sup> The lines of Debye photograph of powdered samples of Au-Cd alloy containing 47.5 atomic pct Cd prepared in this laboratory were identified and agreed fairly well with those of

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Ölander. The crystal structures of the two phases are as follows:<sup>12</sup>

High-temperature phase ( $\beta_1$ ):

CsCl structure, 2 atoms per unit cell, ordered.  
 $a = 3.3165 \pm 0.0005$  kX units.

Low-temperature phase ( $\beta'$ ):

Orthorhombic,  $a = 3.1476$ ,  $b = 4.7549$ ,  $c = 4.8546$ ,  $\pm 0.0005$  kX units.

Two Cd atoms approximately located at 0,0,0  
 $0, \frac{1}{2}, \frac{5}{8}$

Two Au atoms approximately located at  $\frac{1}{2}, 0, \frac{1}{2}$   
 $\frac{1}{2}, \frac{1}{2}, \frac{1}{8}$ .

The Au-Cd alloy containing 49.0 atomic pct Cd undergoes a diffusionless transformation from the ordered body-centered cubic structure to a tetragonal structure<sup>7</sup> when it is cooled to about 30°C; and the reverse transformation typically takes place when the alloy is heated to about 40° to 55°C, depending on the previous history of the alloy. The structural details of the tetragonal phase are not known.

### Experimental Procedure

The back-reflection Laue method was used to determine the orientations of the single crystal  $\beta_1$  phase. The specimen was fixed in a holder provided with means of heating and cooling the specimen without disturbing its position. By this means the orientation relationship between the  $\beta_1$  and  $\beta'$  phases was determined. The transformation markings and the plane of moving interface between the  $\beta_1$  and  $\beta'$  phases during transformation were determined by measuring the traces of the markings across two flat surfaces perpendicular to each other.

The change in resistivity of the Au-Cd single crystals on cooling and heating through the transformation temperature range with and without applied stress was studied. The measurements were obtained by setting the sample in a wedge against two knife edges. A current of about 5 amp was sent through the sample and the voltage drop between the knife edges was measured by a Leeds and Northrup K-2 potentiometer. The current going through the sample was measured by placing a calibrated shunt in series in the circuit and measuring the voltage drop across the shunt with another K-2 potentiometer.

The orthorhombic  $\beta'$  phase possesses a characteristic pseudo-rubberlike behavior. The stress-strain curves of this phase within the quasi-elastic range were also obtained.

Motion pictures, taken at a magnification of 100 diam, were prepared which reveal the changes in surface contour of a metallographically polished single-crystal specimen containing 47.5 atomic pct Cd. These changes in contour make it possible to follow the motion of the interface between the new and old phases, both on heating and on cooling.

### Results

**Orientation Relationships:** The orientation relationships between the  $\beta_1$  and  $\beta'$  phases of the Au-Cd single crystal containing 47.5 atomic pct Cd, from several independent determinations from back-reflection Laue patterns, were found as follows:

$(011)_{\beta_1}$  parallel to  $(001)_{\beta'}$  (planes)

$[\bar{1}\bar{1}1]_{\beta_1}$  parallel to  $[\bar{1}\bar{1}0]_{\beta'}$  (directions).

**Transformation Markings and Moving Interfaces:** In general, a single crystal of the cubic high-

temperature phase  $\beta_1$  does not transform on cooling to a single crystal of the low-temperature phase  $\beta'$ . Instead, the sample is found after transformation to consist of an aggregate of crystals of the low-temperature phase. The relative orientations of these crystals correspond to the various crystallographically equivalent transformation lattice shears. Thus, in general, the transformation of the single-crystal specimen as a whole is inhomogeneous. This is clearly shown by the fact that if a polished flat surface is prepared on the specimen while it is hot, and thus has the cubic structure, this surface is no longer plane after transformation to the orthorhombic structure. If the transformation occurred in a completely homogeneous way, the plane surface of the cubic crystal should remain plane and free of surface markings after transformation. These heterogeneous transformation strains are, however, completely reversed on reheating to the cubic phase. The strain markings disappear and the originally plane surface becomes plane again. In the following this will be referred to as a "multiple interface transformation."

In the present work success has been achieved in producing a transformation from the cubic to the orthorhombic phase by the motion of a single interface. In this case transformation starts at one end of the cubic single-crystal specimen, and then, on continued cooling, the interface between the two phases is translated toward the other end of the specimen. The shear character of the transformation is readily apparent from the appearance of the specimen after partial transformation; the flat surface on the original cubic crystal has become two plane surfaces which intersect in a sharp corner at the interface, and the dihedral angle agrees with that predicted from the lattice shear value from the X-ray diffraction observations. After complete transformation to the orthorhombic structure no strain markings are visible on the polished surface of the sample. This will be referred to here as a "single interface transformation."

The pre-treatment of the crystal sample required to achieve the homogeneous transformation described above includes an anneal of several days a few degrees below the solidus temperature.

The plane of the interface between the two phases during single interface transformation is the (331) of the cubic phase, within the experimental error of approximately 2°.

**Reversible Orientation Relationships:** During the determination of orientation relationships of the transformation, it was invariably found that when a single crystal of  $\beta_1$  transformed by the multiple interface mechanism into a crystal aggregate of  $\beta'$ , on reverse transformation a single crystal of the initial orientation was obtained. The same phenomenon was also observed in the Au-Cd single crystal containing 49.0 atomic pct Cd.

**Resistivity Measurements:** The change in electrical resistivity of the Au-Cd single crystal (containing 47.5 atomic pct Cd) on cooling and reheating through the transformation temperature range

Table I. Temperature of Beginning of Transformation

|              | Cooling, °C   |      | Heating, °C   |      |
|--------------|---------------|------|---------------|------|
|              | $M^{\circ}_s$ | 61.0 | $M^{\circ}_c$ | 73.5 |
| No stress    |               |      | $M_c$         | 66.0 |
| Under stress | $M_s$         | 64.0 |               |      |



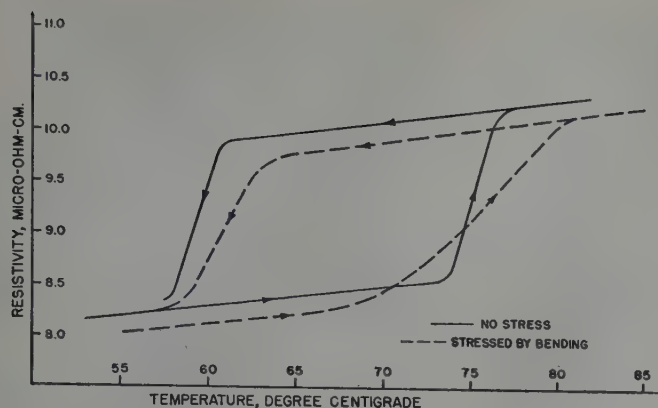


Fig. 1—Resistivity-temperature curve for single crystal Au-Cd alloy containing 47.5 atomic pct Cd.

with and without stress, is shown in Fig. 1. The stress was applied by bending the specimen (approximately  $\frac{1}{8}$  in. sq in cross-section) 0.1 in. (maximum displacement measured at the middle of the specimen) over a span of about 1.5 in. The temperature of beginning of transformation, according to Fig. 1 with and without stress, is summarized in Table I.

The change in electrical resistivity of the Au-Cd single crystal (containing 49.0 atomic pct Cd) on repeated cooling and reheating through the transformation temperature range is shown in Fig. 2. Figs. 1 and 2 were both obtained under conditions of multiple interface transformation.

The electrical resistivity of the 47.5 pct Cd alloy decreases on transformation to the orthorhombic phase while the electrical resistivity of the 49.0 pct Cd alloy increases on transformation to the tetragonal phase.

**Stress-Strain Curves:** A typical load-deformation curve in the bending test of a specimen transformed (multiple interface) from a single crystal of Au-Cd alloy containing 47.5 atomic pct Cd is shown in Fig. 3. The load was applied at the middle of the specimen about  $\frac{1}{8}$  in. sq in cross-section over a span of about 1 in. The load in pounds was plotted against maximum deflection in inches in Fig. 3. The load  $P$ , maximum deflection  $Y$ , modulus of elasticity  $E$ , moment of inertia  $I$ , and the length of specimen between the two supports  $l$ , are related by the following equation:

$$Y = \frac{-Pl^3}{48EI} \quad [1]$$

The effective modulus of elasticity  $E$  of the  $\beta'$  specimen at different stages of bending was calculated according to eq 1 from the respective  $\Delta P/\Delta Y$  values evaluated from the slopes of the small hysteresis loops (see Fig. 3). The calculated  $E$  values are summarized in Table II.

**Motion Pictures of Interfaces:** Motion picture studies of the appearance and motion of interfaces between the  $\beta_1$  and  $\beta'$  phases during transformation were made. These studies included specimens in which the transformation was of the single-interface as well as the multiple-interface kind.

In the case of multiple-interface transformation, plates of the orthorhombic phase appear abruptly during cooling through the transformation range, as is shown in Fig. 4. The rate of formation of these plates is shown here in a succession of four frames from the movie film. The black line extending from

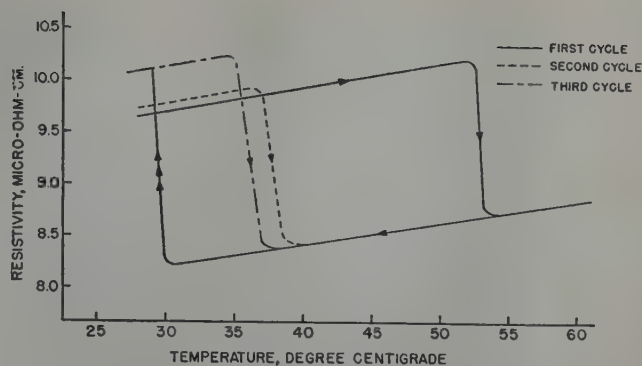


Fig. 2—Resistivity-temperature curve for single crystal Au-Cd alloy containing 49.0 atomic pct Cd.

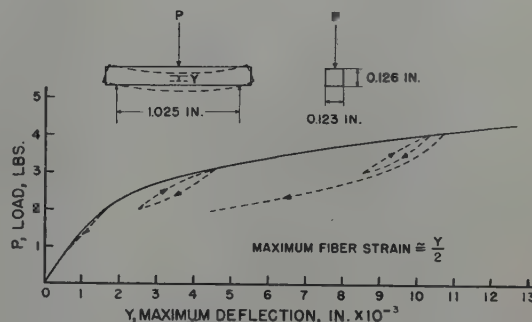


Fig. 3—Load-deflection curve of  $\beta'$  Au-Cd alloy containing 47.5 atomic pct Cd.

the center of the field vertically upward to the periphery is a reference line not belonging to the specimen. No plate extends across the reference line in Fig. 4a. The next frame (Fig. 4b) shows the formation of one plate. The third frame (Fig. 4c) shows the formation of a second plate. In later frames, shown in Fig. 5, these plates grow in thickness and other plates appear which are not parallel to those shown in Fig. 4, until the specimen is apparently completely transformed.

The substantially different state of affairs with the carefully annealed crystal is illustrated in Fig. 6, in which is shown a plane interface between the two phases in a partly transformed crystal. This interface extends completely out to the free surfaces of the specimen. In this case the interface geometry undergoes no obvious change as the transformation proceeds. Correspondingly, the amount of transformed material increases fairly smoothly with time as the specimen temperature is changed. Even in this case, however, there are perceptible irregularities in the interface motion, which are more pronounced for the transformation on heating than on cooling. This homogeneous transformation by slow

Table II. Calculated Values of Modulus of Elasticity of Specimen  $\beta'$

| Load, Lb | Maximum Deflection of Specimen, In. | Maximum Fiber Strain | $E^*$ , Psi        |
|----------|-------------------------------------|----------------------|--------------------|
| 0        | 0                                   | 0                    | $1.5 \times 10^6$  |
| 2        | 0.0015                              | 0.00075              | $1.1 \times 10^6$  |
| 3        | 0.0045                              | 0.00225              | $0.55 \times 10^6$ |
| 4        | 0.0104                              | 0.0052               | $0.61 \times 10^6$ |
| 6        | 0.0345                              | 0.0173               | $0.66 \times 10^6$ |

\* Effective modulus of elasticity averaged over the cross-section of the specimen.



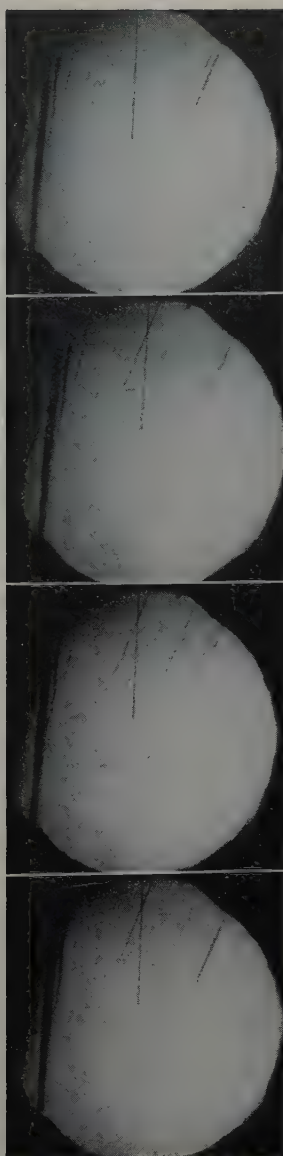
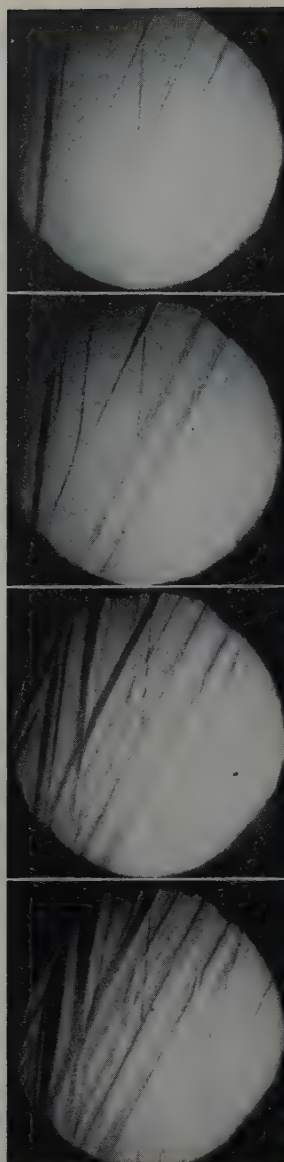


Fig. 4 (left)—Four successive frames showing the formation of  $\beta'$  plates.

Printed from a movie taken at a speed of 32 frames per sec. X100. *a* (top) first frame. *b* (second from top)  $1/32$  after first frame. *c* (second from bottom)  $1/16$  sec from first frame. *d* (bottom)  $3/32$  sec from first frame.

Fig. 5 (center)—Continuation of Fig. 4 showing inhomogeneous transformation of  $\beta_1$  to  $\beta'$ .

X100. *a* (top)—10th frame. *b* (second from top)—50th frame.



*c* (second from bottom)—90th frame. *d* (bottom)—130th frame.

Fig. 6 (right)—Prints taken from a movie film (made at a speed of 32 frames per sec) showing the single interface transformation of  $\beta_1$  and  $\beta'$ .

Moving interface is marked by arrow head. X100. *a* (top)—1st frame. *b* (second from top)—12th frame. *c* (second from bottom)—23rd frame. *d* (bottom)—34th frame.

Figs. 4-6. Area reduced approximately 50 pct in reproduction.

movement of an interface between the two phases is not to be confused with isothermal transformation. The interface moves under the condition that the temperature of the specimen is continuously changing. Preliminary measurements show that the rate of movement of the interface is almost directly proportional to the rate of change of temperature of the specimen. Another phenomenon observed in the case of single-interface transformation is stabilization. When, for instance, the temperature of the specimen is arrested on heating, the interface movement stops and no further transformation occurs until the specimen is heated to a slightly higher temperature than the temperature of arrest.

### Discussion

*Mechanism of  $\beta_1$ - $\beta'$  Transformation:* The atomic movements and crystallographic mechanism in-

involved in the  $\beta_1$ - $\beta'$  transformation of the Au-Cd alloy containing 47.5 atomic pct Cd will be separately discussed in another paper.<sup>12</sup> The crystallographic mechanism was experimentally evaluated as a simple homogeneous shear  $(\bar{3}31)_{\beta_1} [323]_{\beta_1}$  of about  $3^\circ$  plus a possible homogeneous contraction of about 0.015  $kX$  units along the  $b$ -axis of the orthorhombic cell. This crystallographic mechanism yields almost exact agreement between the calculated and experimentally measured values of the cell dimensions of the orthorhombic phase.

*Nucleation:* The effect of stress on the temperature of beginning of transformation illustrated in Fig. 1 shows that nucleation in this diffusionless transformation is strongly influenced by the state of stress present in the specimen. Although the effect of stress on transformation has been discussed



by several investigators, such as Scheil<sup>7</sup> and McReynolds,<sup>8</sup> the data shown in Fig. 1 are the only available data demonstrating the effect of stress during a whole hysteresis cycle.

According to Fig. 1 the effect of the stress distribution on the transformation on heating is somewhat different from its effect on the transformation on cooling. In the first case transformation starts at a lower temperature but goes to completion at a higher temperature than in the stress-free case. On cooling, however, the transformation starts at a higher temperature but goes to completion at approximately the same temperature as it does for the same specimen not under stress. This difference between the effects of stress on the  $\beta_1 \rightarrow \beta'$  and the  $\beta' \rightarrow \beta_1$  transformations can be understood if one considers that a shear stress cannot oppose the transformation from cubic to orthorhombic, but can oppose the reverse transformation. Corresponding to any particular plane and direction of transformation shear, it is possible for the cubic to orthorhombic transformation to occur on the same plane but in the reverse direction. Thus if an applied shear stress opposes transformation in one of these directions, it must aid transformation in the other.

Because of the lower symmetry of the orthorhombic phase, transformation to the cubic phase by simply reversing the direction of shear on a particular plane cannot occur. Now since the specimen on which the data of Fig. 1 were obtained had originally been transformed to the orthorhombic phase by the multiple interface mechanism with no applied stress, the variously oriented regions of orthorhombic phase included some so oriented that the applied stress aided the reverse transformation. These regions accounted for the beginning of transformation at a lower temperature than that observed when no stress is applied to the specimen. Conversely, regions of the orthorhombic phase so oriented that the applied stress opposed the transformation shear transformed at a higher temperature than when no stress is applied. This discussion is, of course, based on the premise that the original cubic single crystal is produced by the orthorhombic to cubic transformation, as has always been observed in this investigation.

On the basis of the above discussion it might be expected that loading the specimen in bending would raise not only the temperature at which the transformation starts on cooling but also the temperature at which it goes to completion. On the other hand, near the neutral axis the stress is low, and correspondingly the material located here will transform at essentially the same temperature as when no stress is applied.

This interpretation of the effect of stress on the transformation characteristics is supported by the observation that was made that a straight rod of the cubic phase acquired a permanent set if it was cooled through the transformation under stress. This permanent set disappeared and the specimen again became straight when reheated to the cubic phase, even when the specimen was still stressed in bending.

Perhaps the most important evidence that this diffusionless transformation is nucleated by residual stresses, or certain types of imperfections, lies in the fact that a specimen which transforms with many interfaces may be made to transform with a single interface (i.e., the formation of an interface at one end of the specimen and movement of this interface

toward the other end of the specimen until complete transformation) by long annealing. Second, a specimen which transforms with a single interface may lose this characteristic by improper handling, only to be brought back again by annealing. These phenomena cannot be readily interpreted by the thermodynamic theory of embryo nucleation recently advanced by Fisher, Hollomon, and Turnbull.<sup>13</sup> It appears rather that the nucleation of the low-temperature phase on cooling is primarily dependent on the existence of imperfections in the specimen which perhaps had their origin in growth from the melt or in previous plastic deformation.

*Transformation with a Single Interface:* The transformation of a well-annealed single crystal of the 47.5 atomic pct Cd alloy by the motion of a single interface from one end of the specimen to the other represents a diffusionless phase change with the simplest possible geometry. The volume of stable phase grows at the expense of the unstable phase by the displacement of a single plane interface of unchanging area. One of the aspects of this transformation which must be accounted for is the fact that it does not proceed isothermally, and, in fact, if a partly transformed specimen is held at constant temperature the interface becomes stabilized against further displacement.

It appears that some relaxation process occurs at or near the interface which lowers the interfacial energy and thus the free energy of the sample. Before this relaxation occurs the free energy of the specimen at constant temperature is a straight-line function of the amount transformed and hence of the position of the interface. After relaxation the graph of free energy as a function of interface position possesses a relative minimum at the actual position of the interface.

This behavior might be likened to the rolling of a steel ball down an inclined plane which is coated with a soft material into which the ball sinks. The ball becomes stuck unless it is rolling rapidly. In the transformation experiments discussed in this paper, however, a rapid motion of the interface is precluded by the latent heat of the phase change. Since the transformation is observed at a temperature only about  $10^\circ$  from the thermodynamic equilibrium temperature at which the bulk free energies are equal, rapid and hence adiabatic transformation is not possible. An upper limit to the rate of transformation is set by the rate at which the latent heat is conducted away. No direct evidence as to the nature of this relaxation process at the interface has yet been obtained.

*Imperfections Caused by  $\beta_1$ - $\beta'$  Transformation:* A typical back-reflection Laue photogram of a  $\beta'$  specimen transformed by the motion of a single interface from a single crystal of  $\beta_1$  is shown in Fig. 7. The spots seem to be sharp and the Laue zones are rather well defined.

In the case of complex transformation with many interfaces, however, the formation of differently oriented regions (see Fig. 5) will give rise to misfits at places where these regions meet. The strain due to these misfits or imperfections presumably causes the phase to follow the opposite path on its reverse transformation to the  $\beta_1$  phase, as is experimentally observed.

The generation of imperfection in the low-temperature phase by diffusionless transformation is reflected in the electrical resistivity data shown in





Fig. 7—Back-reflection Laue photograph of  $\beta'$  crystal transformed with a single interface from a single crystal of  $\beta_1$ . X-ray beam almost parallel to  $[111]$  direction of  $\beta'$ .

Fig. 2 for the Au-Cd alloy containing 49.0 atomic pct Cd: the electrical resistivity of the tetragonal low-temperature phase at a given temperature increases successively after each transformation cycle while the temperature of the reverse transformation to  $\beta_1$  phase decreases successively after each transformation cycle. Both the electrical resistivity of the high-temperature  $\beta_1$  phase (at a given temperature) and the temperature of transformation into tetragonal phase, however, remain unchanged by cyclic cooling and reheating. The electrical resistivity of the tetragonal phase after transformation decreases slowly with time (finally reaching a stabilized value), meanwhile the temperature of reverse transformation to the  $\beta_1$  phase increases, indicating that the imperfections generated in the tetragonal phase become less effective in nucleating the reverse transformation. A similar phenomenon was also observed in the Au-Cd alloy containing 47.5 atomic pct Cd.

The rubberlike properties of the  $\beta'$  orthorhombic phase may be seen from the stress-strain curve shown in Fig. 3. First, it has an extraordinarily low effective modulus of elasticity, about  $1 \times 10^6$  psi; and, second, the effective elastic modulus increases slowly with increasing stress. The most probable explanation of this rubberlike behavior of the orthorhombic phase when it consists of variously oriented regions, all transformed from one cubic single crystal, appears to be that it represents displacement of the interfaces between the differently oriented regions. This displacement is in such a direction that favorably oriented regions increase in size at the expense of less favorably oriented ones. In this connection, "less favorably oriented" means so oriented that the applied shearing stress tends to shear the region back toward the high-temperature cubic structure. When observed under the microscope during bending, changes in surface contour are seen that can be interpreted as interface displacements of this kind.

When the stress applied to the specimen is released, the boundaries between the variously oriented

regions return to their original positions and the specimen regains its original shape.

The origin of the force which makes the interfaces return to their original positions probably is related to a relaxation process which occurs at or near the interfaces between the differently oriented regions. This relaxation process may be essentially the same as that discussed above with reference to the motion of the single interface between the two phases. Additional evidence for this relaxation process is furnished by the observation that immediately after a specimen has been transformed to the orthorhombic phase it is not rubberlike, but is very soft and takes a permanent set. Apparently the boundaries between the differently oriented regions stay in their new positions after the release of the applied stress if they are moved before the relaxation occurs. This permanent set is recoverable, however, for it disappears as the specimen is transformed back to the cubic phase.

The rubberlike behavior was not found in the low-temperature tetragonal phase of the Au-Cd alloy containing 49.0 atomic pct Cd. Apparently this behavior is characteristic of the orthorhombic  $\beta'$  phase.

### Summary and Conclusions

The mechanism of diffusionless transformation in Au-Cd single crystals containing about 50 atomic pct Cd was investigated by means of X-ray analysis of the orientation relationships, electrical resistivity measurements, and motion picture studies of the movement of boundaries between the new and old phases during transformation. The mechanism of diffusionless transformation and the generation of imperfections by diffusionless transformation were discussed. The results of this study also suggest the need of further investigation of the nature of imperfections present in the parent alloy and the type of imperfections generated in the product by diffusionless transformation.

### Acknowledgments

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# Atomic Relationships in the Cubic Twinned State

by W. C. Ellis and R. G. Treuting

The twinned state is characterized by a lattice of coincidence sites. Imperfections are required at stable lateral twin interfaces. Twinned regions can occur with relative ease in the diamond cubic structure.

IN recent contributions<sup>1, 2</sup> on the origin and growth of cubic annealing twins, attention has been directed to the orientation relations between such twinned components and their parent matrix. There are some aspects of twinning which may be illuminated by a more detailed consideration of the twinned state<sup>3</sup> alone. As an extreme example, the dense twinning in cast ingots of germanium,<sup>4</sup> as contrasted with the rarity of twins in cast face-centered cubic metals, is yet to be accounted for. It has been this that has led us to the present work, which, it will be noted, uses methods and constructions in many respects similar to those of Kronberg and Wilson.<sup>1</sup>

In the cubic systems, a  $70^\circ 32'$  rotation about a  $\langle 110 \rangle$  axis is angularly equivalent, as to twinning, to the more usually considered  $180^\circ$  rotation about a  $\langle 111 \rangle$  axis. Figs. 1 and 2 show a  $(110)$  projection of a twinned face-centered cubic lattice and a twinned diamond cubic lattice. In both figures, the two adjacent planes *A* and *B*, shown by the larger and smaller circles, are sufficient to represent the entire array. In each case a section of lattice, the original atom sites of which are shown by open circles, has been rotated as indicated through  $70^\circ 32'$  to bring an original  $[\bar{1}12]$  direction into coincidence with the  $[1\bar{1}2]$  direction. The latter is the intercept on the  $(110)$  projection of the  $(\bar{1}11)$  plane normal thereto, the twinning plane. In the face-centered cubic case the rotation can be performed about an axis passing through an atom-site; the mirror plane then is also a composition plane containing atoms common to both twinned and untwinned lattices.

The diamond cubic lattice may be construed as two interpenetrated face-centered lattices. Its  $\{111\}$  planes recur in a sequence of alternately short and long interspacings. Consequently a mirror plane for twinning cannot be a composition plane, but must be the bisector of one of the spacings. When the longer spacing is selected, the closest distance of approach across the mirror plane in the  $[\bar{1}11]$  direc-

tion is identical with that in the untwinned structure.

In each case periodically recurring  $(\bar{1}11)$  planes (parallel with the twinning plane) are found, on which there is coincidence of atom sites of the pretwinned and twinned orientations; these are indicated by the cross-hatched circles. In the face-centered lattice there is such coincidence every third  $(\bar{1}11)$  plane; in the diamond cubic lattice, on two adjacent planes in every six. At the twinning interface in the latter, there is on each side of the mirror plane a  $(\bar{1}11)$  plane of atoms common to both twin components. Conceivably, there is little influence on a plane of atoms about to be adhered to such a pair of coincidence planes, whether it be laid down in a normal or in a twinned position with respect to the previously formed structure. Slawson<sup>5</sup> has attributed the high incidence of twinning in diamond to this boundary state.

Further examination shows that the motion of intermediate planes can consist of various pairs of equal and opposite translations, for example of  $(\bar{1}11)$  planes in the  $[1\bar{1}2]$  direction, the familiar twinning shear, indicated in the small schematics in the figures. Since the translations form a system of shears of alternating sign between coincidence planes, twinning could take place by such a mechanism over an extended region without extensive shear; in fact, in this case any atom moves but the distance  $a_0/\sqrt{6}$  in the  $[1\bar{1}2]$  direction. One alternative construction for the face-centered cubic lattice leading to the same end result is illustrated in Fig. 3. The plane  $(\bar{1}11)$  with respect to the pretwinned orientation (the twinning plane of Fig. 1) is given, the twinned region arbitrarily bounded by  $\langle 110 \rangle$  and  $\langle 112 \rangle$  directions. The coupled shear is identical to that of Fig. 1. The "rotational" movement about coincidence sites generating the same twinned position could consist as shown of the translation  $a_0/\sqrt{6}$  for each atom of a group of three in the *B* layer in a different one of the three  $\langle 112 \rangle$  directions, and a similar translation of the underlying three atoms in the *C* layer in either the same or the opposite sense. This is not dissimilar to Kronberg and Wilson's construction for their  $22^\circ$  rotation of three adjacent  $\{111\}$  planes.

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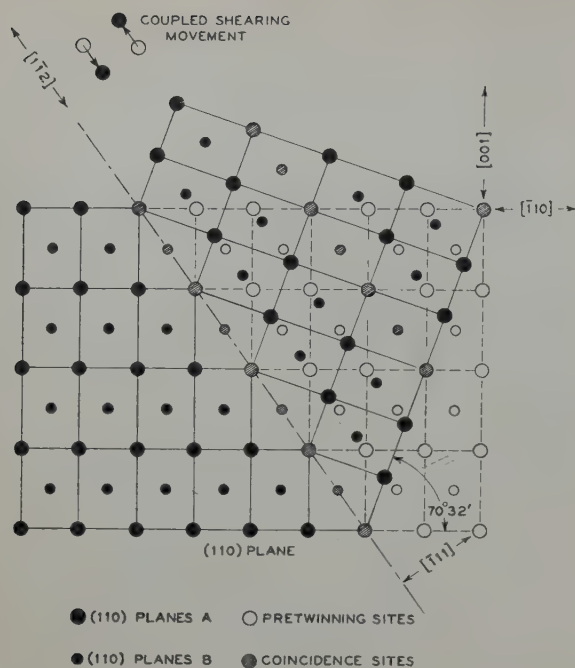


Fig. 1—Face-centered cubic twinning, (110) projection.

On examining the body-centered cubic case, we find an analogous situation: The projection on the (110) plane is given in Fig. 4. The  $(\bar{1}12)$  twinning plane shows coincidence of sites every third layer, with a system of translations which can be coupled in one manner or another to balance within a six-layer identity period. Although there is a coincidence plane every third layer from the twinning plane, these belong alternately to (110) plane sets A and B.

### The Coincidence Site Superlattice

If the projections of twinning in the three cubic systems are examined further, it is found that in each case the twinning plane and a system of others parallel thereto are not the only planes of coincidence sites. There is in each twinned region a superlattice of atom sites common to the pre- and post-twinned orientations.

In the face-centered cubic lattice, Fig. 1, the  $(\bar{1}12)$  plane perpendicular to the twinning plane and to the plane of projection has periodic recurrence of coincidence sites and the same index type in each portion of the twin. These properties are also possessed by the other two  $\{112\}$  and the three  $\{110\}$  planes perpendicular to the twinning plane. A stereographic twinning operation also shows polar coincidence between certain  $\{221\}$  planes of the pre-twinned orientation and  $\{100\}$  of the twinned, and vice-versa; and between respective  $\{511\}$  and  $\{111\}$  planes and vice versa, among others. Under the assumed atomic relationship, these planes are also periodically atomically coincident. In such cases the difference in atomic density dictates that not all the sites of one orientation can belong likewise to the other. Thus, in Fig. 1 the  $(\bar{1}11)$  plane of the twinned region coincides with the sparsely populated  $(1\bar{1}5)$  of the pretwinned orientation. Obviously, only occasional atoms of the former can occupy sites on the latter, but all such sites are so occupied.

The coincidence site superlattice is no more than

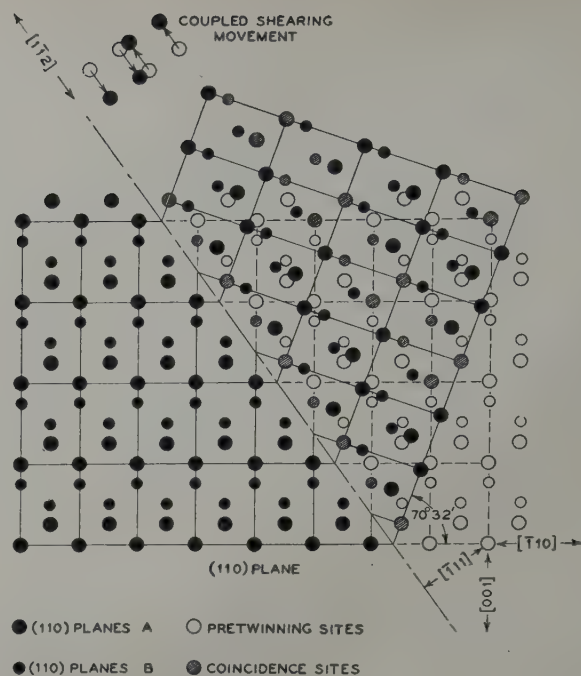


Fig. 2—Diamond cubic twinning, (110) projection.

a possible description of the twinned state in the cubic systems, the coupled shear mechanism a suggestion as to how this state may under some circumstances be attained. Since the mechanism results in a perfect twinning relationship, it would not apply in the case of nucleation from a distorted matrix.<sup>2</sup> It would be a possible mode of twin growth in the course of grain growth following recrystallization only if the twin interface migrated with increasing grain size. Recent evidence by Burke<sup>3</sup> is in opposition to a twin interface migration. Two phenomena demonstrated by Burke, however, may be rationalized by the proposed mechanism: One of these is coalescence, in effect a detwinning mechanism; and the other the rectification of stepped twin boundaries† apparent in Burke's photographs. Each of these effects could be produced by a lateral propagation of the coupled shear mechanism in a direction to minimize the twin boundary area.

### Lateral Interfaces of Twins

In each of these cases, also, the twin has other boundaries than the twinning plane or a grain boundary. Lateral, or incoherent, boundaries are in general straight and, when enough appear in one grain, show few and preferred directions. Hence, they are probably crystallographic planes forming relatively stable interfaces. An interface of this nature might be supplied by any of the planes of the coincidence site superlattice. Each of these is occupied by atoms common to the lattices of both orientations; across such there may be a more or less disperse aggregation of atomic juxtapositions requiring readjustment to satisfy nearest neighbor distance requirements.

Thus, if as in Fig. 3, a twinned region be projected on a  $\{111\}$  twinning plane and bounded from the untwinned material by planes of the  $\{110\}$  and  $\{112\}$  types (normal to and intersecting the  $(\bar{1}11)$  projection plane in  $\langle 112 \rangle$  and  $\langle 110 \rangle$  directions respec-

† Observed by Burke. We are indebted to Dr. Burke for the opportunity to read his manuscript prior to publication.



tively), then the three  $\{112\}$  planes are seen to consist completely of coincidence sites, and atoms paired across this plane lie  $a_0/\sqrt{6}$  mutually distant. The three  $\{110\}$  planes are but  $1/3$  populated by coincidence sites and the remaining atoms are at the  $a_0/\sqrt{6}$  distance from their nearest neighbors in the untwinned region. (Greninger<sup>7</sup> has reported a  $\{110\}$  lateral twin boundary in copper.)

From the atom displacement it appears that, in twinning a perfect lattice, this close juxtaposition must be realized across any lateral boundary plane in the absence of any relieving mechanism. Since the  $a_0/\sqrt{6}$  interatomic spacing corresponds to a compressive strain of 0.423 from the normal distance of closest approach, it is plausible to consider that this circumstance does not in fact occur. Accepting this as an hypothesis, we are led to the conclusions:

Crystallographic lateral twin boundaries are sites of lattice imperfections to relieve the violation of nearest neighbor requirements otherwise occurring there. Lateral twin growth will tend to proceed until an advancing boundary generates or encounters a sufficient concentration of lattice imperfections to permit a relatively stable interface. The most probable lateral twin boundary is that requiring a minimum number of lattice imperfections to render it relatively stable. This condition is approached by a crystallographic interface having a maximum frequency of coincidence sites and a minimum frequency of nearest neighbor distance violations, but planes meeting the one criterion do not in general tend to satisfy the other.

Remarkably, this close atomic juxtaposition across potential lateral twin boundaries seems to be avoided in the diamond cubic lattice. If now in Fig. 2 we consider the twinned region to be further bounded by a  $(\bar{1}\bar{1}2)$  plane passing through coincidence sites, the closest approach of atoms in the twinned and untwinned material across this boundary is again

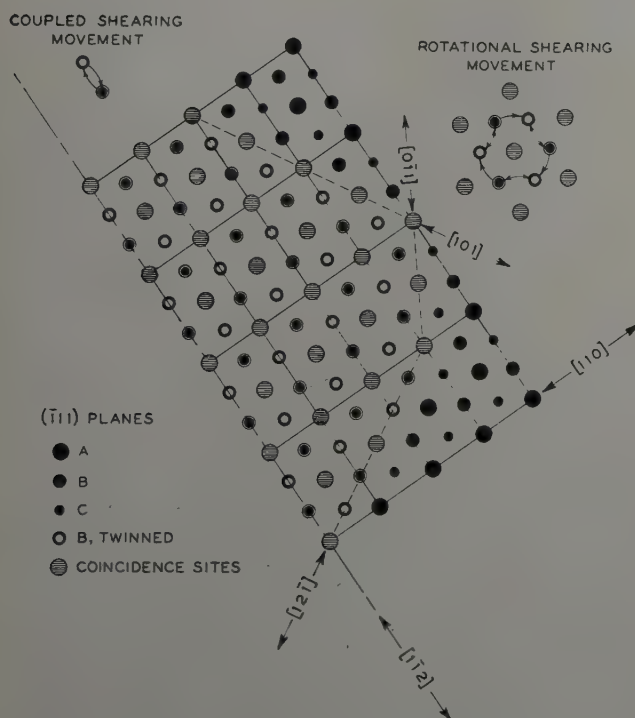


Fig. 3—Face-centered cubic twinning,  $(\bar{1}\bar{1}1)$  projection.

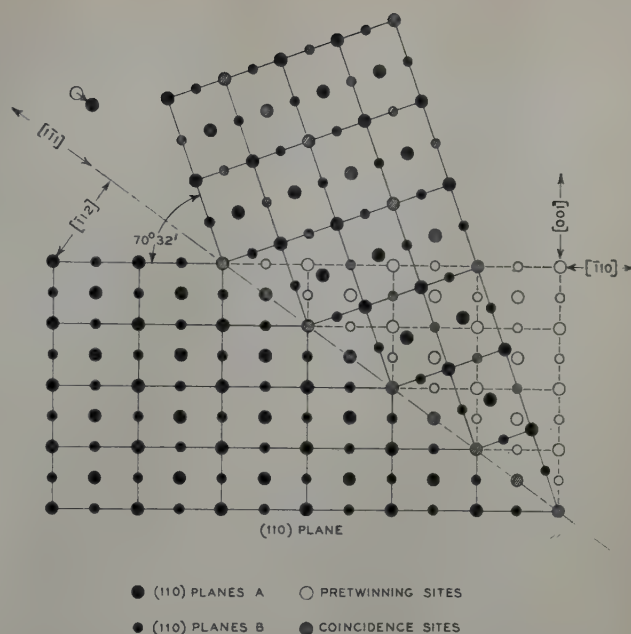


Fig. 4—Body-centered cubic twinning,  $(110)$  projection.

$\frac{a_0}{\sqrt{6}}$ . The normal closest approach in this structure is  $\frac{a_0\sqrt{3}}{4} = 0.433 a_0$ ; the strain between atoms across such a lateral twin boundary is but  $-0.058$ . However, under this construction atoms on the coincidence plane have alternately three and five nearest neighbors, a circumstance that presumably requires some adjustment and consequent strain along such a boundary. Yet the favorable trans-boundary spacing, together with the double layer of coincidence sites at the twin plane in the diamond lattice, one is inclined to associate with the multitudinous twins found in cast silicon and germanium.<sup>4</sup>

## Summary

Twinning in cubic metals can be the result of small atom displacements of a fraction of an interatomic distance on planes lying within a coincidence site superlattice. No extensive shear is required.

Imperfections are required in a stable lateral twin boundary in order to satisfy nearest neighbor distance requirements across such boundaries.

A double layer of coincidence sites along twin planes and a favorable lateral (or incoherent) trans-boundary spacing in the diamond cubic lattice pre-disposes materials having this structure to twinning.

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# Transitions in Chromium

by M. E. Fine, E. S. Greiner, and W. C. Ellis

Discontinuous changes of Young's modulus, internal friction, coefficient of expansion, electrical resistivity, and thermoelectric power are evidence for a transition in chromium near 37°C. Although the X-ray diffraction pattern gives no clue, a difference between the thermal expansivity and the temperature dependence of the lattice parameter suggests a crystallographic change. Young's modulus data disclosed another transition near -152°C.

THE thermal dependence of a number of properties of chromium indicates a transition occurring over a temperature range near room temperature. Bridgman<sup>1</sup> noted this first from a minimum in the electrical resistivity near 12°C. In a sample of greater purity, Söchtig<sup>2</sup> observed the minimum at 41°C. Erfling<sup>3</sup> reported an inflection in the thermal expansivity curve at 36°C. These temperature-dependence curves are reversible with no hysteresis being detected. No discontinuity or inflection has been observed in the heat capacity<sup>2</sup> or the paramagnetic susceptibility.<sup>2</sup> Likewise, no one has noted a change in crystal symmetry.

In the present investigation Young's modulus, internal friction, coefficient of expansion, electrical resistivity, illustrated in Fig. 1, lattice constant, Fig. 2, thermal electromotive force, Fig. 3, and paramagnetic susceptibility, Fig. 4, were measured over an extended temperature range.

The samples were prepared in two ways: (1) By cold pressing a sintered electrolytic powder compact,<sup>4</sup> and (2) by electroforming from an aqueous solution. The electroformed samples were prepared by R. A. Ehrhardt and G. Bittrich by plating on copper or nickel tubes from an aqueous solution according to the method of Brenner, Burkhead, and Jennings.<sup>5</sup> The pressed powder samples (method 1) were finally annealed at 1400°C in purified helium; the electroformed samples, packed in powdered chromium, were vacuum-annealed at 1000°C.

From the composition of the original powder<sup>4</sup> the purity of the pressed powder samples is estimated to be 99.8 pct Cr. Spectrochemical analysis furnished by E. K. Jaycox, revealed only slight traces of impurities in the electroformed sample (less than 0.001 pct), neither iron nor nickel being detected. Chromium deposited by this method is reported to contain approximately 0.05 pct O.<sup>6</sup>

## Methods and Data

**Young's Modulus:** For measurement of Young's modulus, an annealed, pressed powder sample, 0.114 x 0.237 x 1.845 in., and an electroformed sample, 0.10 in. od, 0.01 in. id, and 1.86 in. long, were prepared. The resonant frequencies of the rod samples in forced longitudinal vibration were measured at a series of temperatures from -192° to 200°C by a method previously described.<sup>6, 7</sup>

Because the samples were nonferromagnetic, iron-

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silicon or molybdenum permalloy tips (0.013 in. thick) were soldered to the ends. The softening temperature of the solder limited the temperature of measurement. Young's modulus,  $E_T$ , of chromium at temperature,  $T$ , may be calculated from the resonant frequency of the composite rod,  $f_T$ ; the thickness of the tips,  $t$ ; the length of the chromium sample at 25°C,  $l_c$ ; the density of chromium at 25°C,  $\rho_c$  (7.20 g per cc);<sup>8</sup> and the thermal expansivity,  $\Delta l/l_{25}$ . Modulus differences for two temperatures,  $E_T$  and  $E$ , are accurate to  $\pm 0.002 \times 10^{11}$  dynes per cm<sup>2</sup>.

$$E_T = 4\rho_c(l_c + 2t)^2 f_T^2 \left(1 - \frac{\Delta l}{l_{25}}\right)$$

Young's modulus at 25°C, Fig. 1a, is  $28.2 \times 10^{11}$  dynes per cm<sup>2</sup> ( $40.8 \times 10^6$  psi) in wrought chromium (upper curve). The modulus of the electroformed sample is apparently lower due to cracks. From the modulus measurements two transitions were observed: one with a critical temperature at 37°C, the other at -152°C.

**Internal Friction:** The internal friction,  $1/Q$ , was determined from the width,  $\Delta f$ , of the strain amplitude-frequency curve at 0.707 times the strain amplitude at resonance;<sup>7</sup> the internal friction,  $1/Q$ , then equals  $\Delta f/f$ . Fig. 1b shows a sharp peak in internal friction at 38°C. The internal friction of the electroformed sample had a similar maximum.

**Thermal Expansion:** The expansivity measurements, shown in Fig. 2, covering the temperature range -195° to +400°C were made by D. MacNair in an interferometric dilatometer<sup>8</sup> using a sample consisting of three pyramids 0.25 in. high prepared from wrought electrolytic chromium. Below -120°C the experimental points deviated up to  $\pm 2 \times 10^{-5}$  from the drawn expansivity curve in Fig. 2 because of decreased precision of the quartz wedge thermometer at low temperatures. Near 38°C the thermal expansivity curve, Fig. 2, goes through an inflection corresponding to a minimum in the coefficient of expansion, Fig. 1d, and a relative volume decrease on heating.

**Electrical Resistivity:** The variation of electrical resistivity with temperature measured by the potentiometric method is also shown in Fig. 1. The resistivity of the wrought chromium (upper curve) at 20°C is 13.6 microhm-cm; of electroformed chromium (lower curve) 12.8 microhm-cm. The lower value reflects higher purity and agrees closely with a published value.<sup>5</sup> A minimum at 40°C occurs in the resistivity curves of both samples. No conclusive evidence for a transition near -150°C was observed, but the points, Fig. 1, appear to deviate from a smooth curve between -120° and -160°C.



**Crystal Structure:** The structure of wrought chromium was investigated by the powder method in a Debye-type camera. The specimen consisted of powder filings cleaned magnetically and annealed 2 hr at 800°C in vacuum. At -190°C, chromium was found to have the same structure as at room temperature, body-centered cubic.

The lattice constants of the powder specimen were measured between -2° and 58°C in a back-reflection focusing camera.<sup>9</sup> A current of either cooled or warmed helium controlled sample temperature. Chromium  $K\alpha_1$ ,  $\alpha_2$ , and  $\beta$  (211) reflections (Siegbahn 1931) corrected for refraction<sup>9</sup> and systematic errors<sup>10</sup> were used. The precision of individual determinations is 0.003 pct. The lattice constants in Angström units<sup>11</sup> ( $10^{-8}$  cm) are plotted in Fig. 2 (inset).

The lattice constants calculated from 0°C using the thermal expansivity are shown by the dashed curve Fig. 2 (inset). The differences between the observed and calculated values, although small, appear significant and will be discussed.

**Thermal Emf and Thermoelectric Power:** The thermal emf of the chromium (electroformed)-platinum couple was measured between -200° and 103°C with the reference junction at 0°C. In the results, Fig. 3, a positive emf signifies positive current is passing from platinum to chromium at their variable-temperature junction. The slope of the thermal emf curve (thermoelectric power) shows an abrupt change at 40°C, Fig. 3.

**Paramagnetic Susceptibility:** The paramagnetic susceptibilities of an electroformed chromium tube and unannealed electrolytic chromium powder were measured at a series of temperatures, Fig. 4, by F. J. Morin. In the method, the pull of an electromagnet of known field gradient on the sample was measured with an analytical balance. The maximum flux density in the field was 5000 gauss. Spectrochemical analyses of the samples gave no trace of ferromagnetic impurities. The powder sample, however, was visibly oxidized.

The results for the two samples, shown in Fig. 4, disclose no evidence for transitions near either -152° or +37°C. (The spread among the points can be reasonably ascribed to experimental error.) The different slopes appear to be connected with the sample purity—the higher purity material has the larger positive susceptibility coefficient. Söchtig's values for electrolytic chromium powder of unstated purity agree closely with those obtained in this investigation for similar powder.

### Nature of the Transitions

From the four curves of Fig. 1, a good deal can be concluded about the transition near room temperature. It takes place over a large temperature range, progresses only as temperature is changing, within the experiment is independent of the rate of heating and cooling, and is reversible with no hysteresis being detected. (After heating the electroformed sample to 207°C, a stable modulus-temperature curve was obtained, Fig. 1.) On heating, the transition (Fig. 1) begins at approximately -20°C, increases in intensity to a critical value near 37°C, but is not complete until approximately 140°C.

Evidence for the transition near -150°C has been observed only in Young's modulus, Fig. 1. The modulus effect, taking place between -160° and -120°C with a critical temperature at -152°C, is

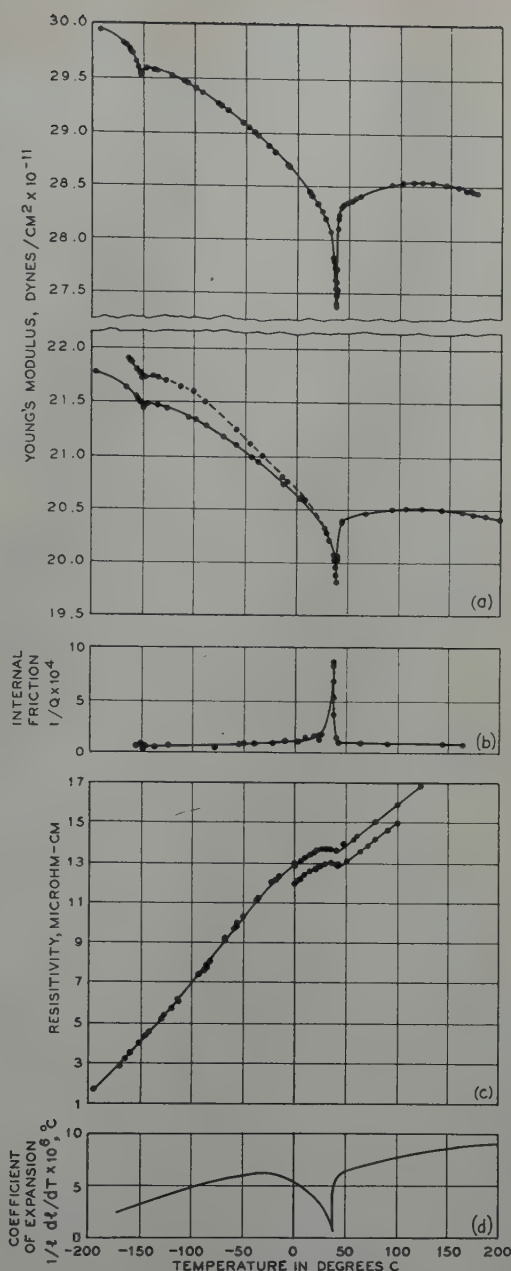


Fig. 1—Thermal dependence of some properties of chromium.

a. Young's Modulus ( $1 \frac{\text{dyne}}{\text{cm}^2} = 1.4504 \times 10^{-5} \frac{\text{lb}}{\text{in}^2}$ ).

Upper curve, wrought electrolytic sample.

Lower curve, electroformed sample.

Dashed curve, before being heated to 207°C.

b. Internal friction (wrought electrolytic sample).

c. Electrical resistivity.

Upper curve, wrought electrolytic sample.

Lower curve, electroformed sample.

d. Coefficient of expansion (wrought electrolytic sample).

similar to the one near room temperature but is of much smaller magnitude.

These transitions in chromium occurring over a temperature range and without hysteresis are akin in pure metals to loss of ferromagnetism. Chromium, however, is not ferromagnetic. The small, almost constant paramagnetic susceptibility (Fig. 4) means that probably neither of the transitions are loss of antiferromagnetism.<sup>12</sup> The overlapping 4s and 3d bands in chromium suggests the transitions involve the ratio of 4s to 3d electrons. From the relative decrease in electrical resistance on heating through the transition near room temperature, Söchtig<sup>2</sup> postulated that the proportion of 4s to 3d



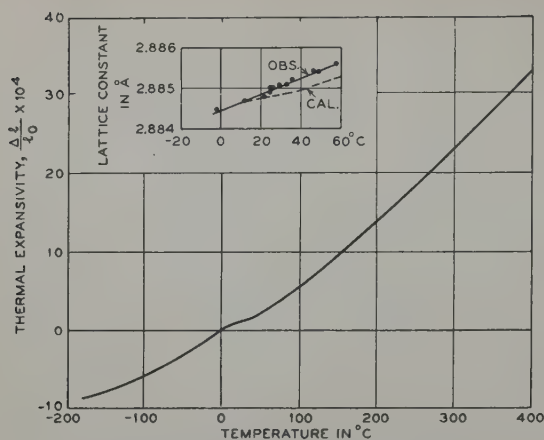


Fig. 2—Thermal expansivity and thermal dependence of lattice constant in wrought electrolytic chromium.

electrons, that is, the relative number of carriers, is increasing. The lack of hysteresis seems to require an electronic change of this kind. The temperature course of the transition would depend upon the electronic energy considerations determining the ratio of 3d to 4s electrons.

Referring to the transition near room temperature, the inflection in the expansivity curve, Fig. 2, is equivalent, on heating, to a decrease in sample length of approximately  $2 \times 10^{-4}$  in. per in. or, assuming isotropic expansion characteristics, a decrease in volume of  $6 \times 10^{-4}$  per in.<sup>3</sup> Because of this volume effect, increasing the pressure would be expected to lower the transition temperature. This has been observed, for Bridgman<sup>1</sup> found that increasing the pressure from 0 to 4000 kg per cm<sup>2</sup> decreased the temperature of minimum resistivity from 12° to -20°C. The transition is also influenced by sample purity. In a number of impure samples Hidnert<sup>13</sup> observed a lower temperature range and a larger volume effect.

On heating through the transition, Young's modulus is larger than the value obtained by extrapolating from below the transition, Fig. 1a. The increase in modulus may be regarded as arising from a difference between the  $U(r)$  relations at high and low temperatures (the modulus is proportional to  $\partial^2 U / \partial r^2$ ). With increasing temperature the  $U(r)$  relation (as in loss of ferromagnetism<sup>14</sup>) gradually changes from that of the low-temperature "modification" to that of the high-temperature "modification." From this consideration alone the modulus is expected to increase gradually through the transition. The observed initial negative deviation of

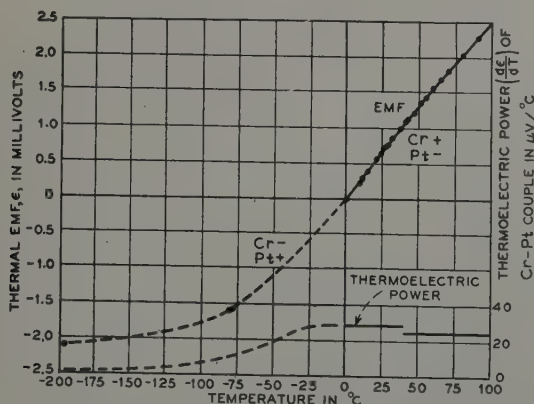


Fig. 3—Thermal emf and thermoelectric power of electroformed chromium (Cr-Pt couple).

Young's modulus from a usual temperature dependence, Fig. 1, implies an additional contribution to the strain. The additional strain may arise as follows: On heating through the transition there is a negative volume effect with the largest change in coefficient near the temperature of minimum modulus (37°C). The additional strain like this volume effect (compare Figs. 1a and d) increases with temperature to 37°C then abruptly decreases. In this temperature region the ratio of the two "modifications" or the completeness of the transition may well be stress-dependent. A tensile stress will then cause the transition to progress in that direction which increases the volume (toward the low-temperature "modification") and the opposite will hold for a compressive stress. The resulting volume changes give larger tensile and compressive strains. The increased internal friction at 37°C, Fig. 1b, is further evidence for a mechanism of this sort.

The difference between the observed lattice constants and those calculated from the expansion data (Fig. 2) suggests the transition involves a departure from the ideal body-centered cubic arrangement. Direct evidence of this departure has not been observed. The difference corresponds to 0.04 pct more atoms (on the average) associated with a unit cell

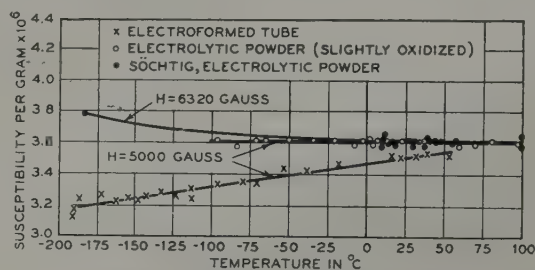


Fig. 4—Paramagnetic susceptibility of electrolytic chromium.

above the transition than below and an equal decrease in the proportion of unit cells. The denser packing is consistent with the observed overall increase in Young's modulus on heating through the transition. The extra atoms by short range movements perhaps assume interstitial (face-centered) positions giving the denser packing. Alternatively, denser packing could arise from disappearance of vacant lattice sites on heating.

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# Effect of Heat Treatment on the Electrical Properties of Germanium

by H. C. Theuerer and J. H. Scaff

Germanium may be reversibly converted from *n* to *p* type by heat treatment. Data for the conversion and the associated changes in resistivity are given and the results are interpreted in terms of changes in the donor-acceptor balance.

**M**EANS for controlling the electrical properties of germanium in a predictable manner are of interest because of the increasing utilization of this element as the semiconducting material in electrical devices. Since both the mechanism and the magnitude of the electrical conductivity depend upon the kind and quantity of impurities present, the conductivity usually is adjusted by first carefully purifying the germanium, and then, by standard alloying procedures, adding the elements desired. The elements usually added are from the third or fifth periodic groups depending upon whether *p*- or *n*-type germanium is desired. However, in the development of germanium rectifiers during the war, it was found that it was possible also to modify reversibly the conductivity of germanium and even to produce conversion from *n* to *p* type by heat treatment.<sup>1,5</sup> Since then a detailed study of this effect has been made. The data are presented in this paper and an explanation is offered for the effects observed.

## Preparation and Experimental Procedure

The method used in preparing the germanium ingots for this investigation has been previously described.<sup>1</sup> The method consists essentially of (1) reduction of  $\text{GeO}_2^*$  and (2) preparation of a 50-g

ingot from the reduced material. Graphite containers are used in both steps. In the first step the  $\text{GeO}_2$  is reduced in hydrogen at  $650^\circ\text{C}$  to form a sponge germanium which, to assure complete reduction and to obtain massive materials, is fused subsequently in the reduction furnace by gradually raising the temperature to  $1000^\circ\text{C}$ . The button of germanium thus obtained corresponds to a yield of 99.8 pct. The final ingot is prepared by fusion of the germanium button in a helium atmosphere. A cylindrical crucible in a vertical silica tube furnace is employed and the crucible is heated by an external induction coil. The ingot is solidified from the bottom upward by raising the induction coil at a constant rate with power to the coil kept at a fixed value.

In such ingots, segregation is normal and most of the impurities are concentrated in the last region of the ingot to freeze. It follows then that the major portion of the ingot is purer than it would have been if freezing had occurred in a random fashion. Moreover the orderly advance of the freezing surface during solidification establishes in the ingot a succession of surfaces of constant composition, if it is assumed that the liquid is homogeneous and that diffusion in the solid is negligible. Therefore, some information on the distribution of impurities in the ingot may be acquired by determining the shape of the solid-liquid interface at different stages of solidification. This is of importance because the concentration of impurities will be seen to affect the response of germanium to heat treatment. Such information is difficult to acquire by direct means, for the impurities responsible for the electrical properties of germanium prepared in this way are present

\* Rectifier grade, prepared by hydrolysis of redistilled  $\text{GeCl}_4$ . Obtained from the Eagle Picher Co.

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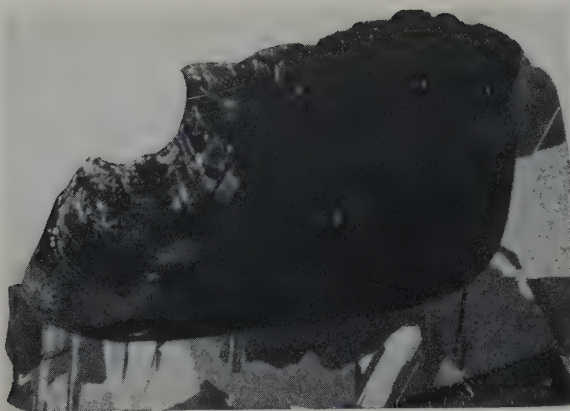


Fig. 1—Shape of solid-liquid interface during the solidification of a germanium ingot.

a (above)—Initial stage.  
b (right)—After ingot is half solidified.



to the extent of only a few parts in ten million and are thus beyond the range of the usual methods of analysis.

The shape of the solid-liquid interface may be determined by preparing ingots in the standard way except that after allowing solidification to proceed for the desired time the crucible is upset to allow the remaining liquid to flow out quickly. Sections of such ingots, etched to reveal the grain structure, are shown in Fig. 1. It will be noted from these that the freezing surfaces are quite smooth and regular and that there is no sign of dendrite growth. Also it may be seen that, while solidification occurs predominately from the bottom of the crucible upwards, there is sufficient heat loss from the sides of the crucible that solidification occurs to some extent from the sides of the crucible inward. This accounts for the curvature in the solid-liquid interface.

For the heat-treating studies the 50-g ingots were cut in half through the vertical axis and from the central portion of one half of the ingot a rectangular specimen  $\frac{1}{8} \times \frac{1}{8} \times 1$  in. was cut, so that the long axis of the specimen was approximately parallel to the vertical axis of the ingot. This specimen was used for resistivity measurements by a potentiometric method. The remaining half of the ingot was used for rectification measurements. To prepare the ingot for these measurements, a large area electroplated contact was made to the rounded surface of the ingot. The cut face of the ingot was then ground flat with abrasive, etched and the surface explored with a tungsten point under a controlled load. By measuring the current through the contact when the direction and magnitude of the applied voltage was changed, it was possible to differentiate quickly between *n*- and *p*-type germanium. Typical rectification patterns obtained in these tests are shown in Fig. 2.

The rectification pattern of Fig. 2 for *n*-type germanium is typical of that of a "high back" voltage rectifier. It will be noted that in the reverse direction (Ge positive with respect to the point) little current flows even at voltages as high as 50v. With increasing applied voltage, larger currents flow and a value is finally reached where further increases in voltage result in a reduced potential drop across the rectifying junction. The peak voltage which the

junction will support is one way of characterizing the properties of germanium as will be seen in the following section.

The half section of the ingot and the companion resistivity specimen prepared as described were heated at successively higher temperatures between 500° and 900°C for periods of 24 hr in a quartz tube in which a helium atmosphere was maintained. After each treatment the specimens were rapidly cooled to room temperature by removing the quartz tube from the furnace and allowing it to cool in still air. The surfaces of the specimens then were ground and etched prior to measurement of the conductivity type and resistivity. At several of the temperatures after the initial 24-hr treatment, the specimens were reheated for an additional 48 hr and the conductivity type and resistivity were remeasured. No significant changes were observed as a result of the second treatment, indicating that a steady state is reached at these temperatures in a 24-hr period. After the samples had been treated at 900°C, they were reheated at several lower temperatures between 900° and 400°C for 24 hr each, again measuring the properties after each heat treatment.

#### Effect of Heat Treatment on Conductivity

In the as-cast state the germanium ingots are *n* type throughout with peak reverse voltages ranging between 50 and 200 v depending on position in the ingot. This is illustrated schematically for ingot sections in Fig. 3, in which the contour lines show regions in the ingot which have the peak reverse voltages listed. The similarity in shape between the contours of peak reverse voltage and the contours of the freezing surface at different stages in solidification, given in Fig. 1, is at once apparent. The peak reverse voltage is highest near the bottom of the ingot and lowest near the top of the ingot. From this it is evident that the peak reverse voltage of the germanium is systematically related to its purity.<sup>2</sup>

If the germanium ingot is heat treated at temperatures above 550°C and cooled to room temperature, in the manner previously described, part of



the ingot transforms to *p*-type germanium. Such material has a poor rectification characteristic with tungsten points, and does not support high voltages in either direction. The regions of the ingot which transform from *n* to *p* type as a result of the various heat treatments and the peak-voltage contour lines for the untransformed *n*-type regions are also given in Fig. 3. It should be recalled that, because of the solidification procedure used in preparing the ingots, the purity decreases progressively from bottom to top of the ingot. The data of Fig. 3 show that the purer material in the ingot converts to *p* type at the lowest temperature of treatment. Higher temperatures of treatment are required to convert those regions in the ingot of lower purity. The general curvature of the *n/p* boundaries after heat treatment suggests again that these are regions of equal purity formed during the freezing process. It will be noted that even at temperatures as high as 900°C, the impurity-rich top of the ingot is not converted to *p* type.

The thermal conversion of germanium from *n* to *p* type is completely reversible. Fig. 3 shows, for example, that the amount of *p* material in the ingot and the peak-voltage contours are the same after a 600°C treatment, whether or not the sample had previous high-temperature treatments. Also, although the specimen had been treated for a total of 96 hr, a final heat treatment at 500°C resulted in material having the same characteristics as that after the initial 500°C treatment. This would not be expected if a substantial diffusion of the impurities initially in the ingot had occurred during the course of the treatments.

Large changes in resistivity are also produced by the heat treatment. Resistivity data for materials from three positions in an ingot are given in Fig. 4. Several features of the curves are to be noted. The resistivity is highest for the purer material at the bottom of the ingot and lowest at the top. As the temperature of treatment increases, resistivity rises reaching a maximum at the *n/p* conversion point. For higher temperatures of treatment the resistivity falls rapidly and reaches a relatively low value after treatment at 900°C. The divergence in the three curves tends to decrease for the higher temperatures of treatment. The resistivity after treatments between 500° and 900°C is independent of previous thermal history and depends only on the final temperature of treatment and on the location of the material in the ingot. Finally the transition temperature for *n/p* conversion increases as the impurity level increases.

Other experiments had shown that the resistivity had reached a constant value after treatment at 500°C for 24 hr. For lower temperatures of treatment, the changes occur much more slowly as shown by data for treatments for various periods of time at 360° and 400°C. For both series of measurements the specimens were first heated to 900°C for 24 hr and rapidly cooled to obtain *p* germanium. They were then reheated at 360° or 400°C for different intervals of time, cooled to room temperature, and measured. These data are given in Table I and in Figs. 5 and 6.

With increasing time of treatment at 360°, a gradual increase in resistivity is observed and after 1084 hr of treatment the upper third of the specimen transformed to *n* type. At 400°C the material is converted to *n* germanium after 24 hr. At this temperature about 500 hr are required for resistivity to

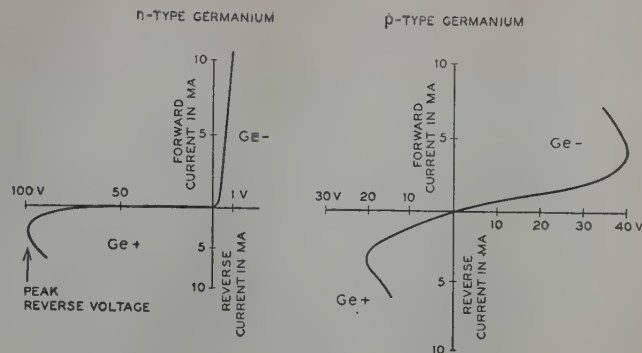


Fig. 2—Typical rectification patterns for *n* and *p* germanium with tungsten point contacts.

reach a constant value. It is to be noted that the terminal values of resistivity after treatment for 1000 hr at 400° are the same as those obtained initially after treatment at 500°C for 24 hr.

### Proposed Mechanism for the Effect of Heat Treatment

It is now well established for both silicon and germanium that *p*-type or *n*-type conduction results if impurities from the third (acceptors) or fifth (donors) periodic groups respectively are present.<sup>3</sup> The conductivity at room temperature is proportional to the number of impurity atoms present. *P*-type conductivity may also result from acceptor levels introduced by lattice defects produced, for example, by physical displacement of germanium atoms from their normal lattice sites.<sup>4</sup> Moreover if donor and acceptor levels occur simultaneously, a compensating action occurs so that the mechanism and magnitude of conductivity depends upon which carrier is in excess and on its net concentration. It is apparent, therefore, that the changes in the properties of germanium on heat treatment are due to a change in the donor-acceptor balance. If we assume, for example, that the concentration of acceptors depends upon the temperature of heat treatment, then for *n*-type material, as the temperature of heat treatment is increased, the acceptor concentration rises and the net donor concentration falls so that an increase in resistivity is observed. The resistivity reaches a maximum after treatment at

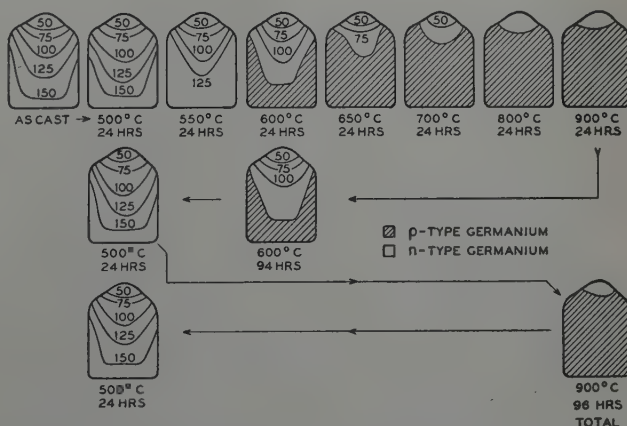


Fig. 3—Effect of different heat treatments on the conductivity type of germanium.



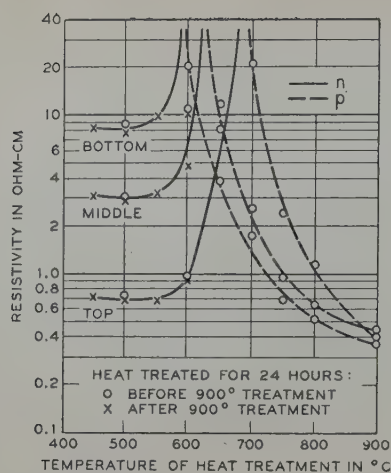


Fig. 4—Effect of temperature of treatment on the resistivity of germanium from different positions in an ingot.

the temperature where the donors and acceptors just balance or compensate one another. For treatments above this temperature acceptors are in excess and the material is *p* type, and, since the acceptor concentration continues to increase with increasing temperature of heat treatment, the resistivity accordingly decreases. This hypothesis adequately explains the shape of the curves of Fig. 4 and the same argument may be used to explain the curves of Fig. 6. Following the argument further it would be expected that the temperature of conversion from *n* to *p* type would be lowest for material with the lowest initial concentration of donors. This is actually the case as shown by the curves of Fig. 4. This also explains the variation in resistivity with location found in ingots heat treated so that the lower part is *p* type and the upper part *n* type (e.g., the 600° treatment, Fig. 3). In this case the resistivity of the *p*-type material is low at the bottom of the ingot and increases as the

*p/n* boundary is approached. The resistivity then falls as the top of the ingot is approached. It is believed that treatment at 600°C increases the acceptor concentration uniformly in the ingot just enough to convert the bottom portion of the ingot to *p* type. In this region of the ingot the concentration of acceptors must exceed that of the donors. Since, however, the donor concentration increases with height in the ingot, the excess of acceptors over donors in the *p* region decreases with height. Hence the resistivity rises in this region as the *p/n* boundary is approached. Above the boundary, the donor concentration exceeds that of the acceptors and in this region the concentration of donors in excess of the acceptors increases progressively with height in the ingot. The resistivity accordingly decreases with height in the *n* region.

The essential feature of the above explanation is that the number of acceptor levels or "holes" depend upon heat treatment. Two mechanisms by which this could occur are known. In the one mechanism, essentially chemical in nature, heat treatment is supposed to change the effective concentration of acceptor impurities as, for example, by a change in solubility with temperature. The other mechanism

Table I. Effect of Heat Treatment at 360°C on the Resistivity of *p*-type Germanium Obtained by Thermal Conversion at 900°C

| Time at 360°C, Hr | Resistivity at Locations in Ingot Indicated |                |                |
|-------------------|---------------------------------------------|----------------|----------------|
|                   | Top, Ohm-cm                                 | Middle, Ohm-cm | Bottom, Ohm-cm |
| 0                 | 0.56                                        | 0.50           | 0.33           |
| 24                | 0.65                                        | 0.73           | 0.45           |
| 114               | 1.05                                        | 1.25           | 0.72           |
| 330               | 2.35                                        | 3.06           | 2.00           |
| 1,084             | 1.54*                                       | 6.88*          | 11.56          |

\* Material converted to *n* type.

is essentially physical in nature. It has been shown<sup>4</sup> that bombardment of germanium by nucleons converts *n* germanium to *p* type and that the converted material may be transformed to the original *n* type by heat treatment at low temperatures. The bombardment is supposed to break the valence bonds by displacement of atoms in the lattice to form defects or "holes" which compensate the existing donors and ultimately result in conversion to *p* type. Beyond the conversion point further bombardment introduces additional defects which further increase the conductivity. According to this view, heat treatment at low temperatures, of the order of 500°C, allows these defects to be "healed" with reversion to the original properties. If the defects created by heating the germanium to temperatures above 500° are retained on cooling to room temperature, then this physical mechanism would also account for the results of the present investigation. Additional experiments are required to determine which of these mechanisms is correct.

### Summary

It has been shown that germanium may be reversibly converted from *n* to *p* type with accompanying changes in resistivity by appropriate heat treatment. The results have been interpreted in terms of changes in the balance between acceptors and donors resulting from an increase in acceptor

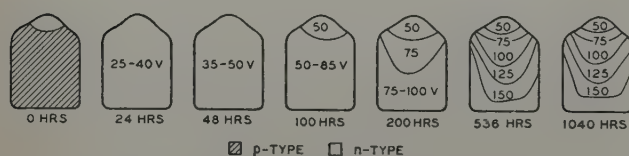


Fig. 5—Effect of heat treatment at 400°C on the conductivity type and peak reverse voltage of thermally converted *p*-type germanium.

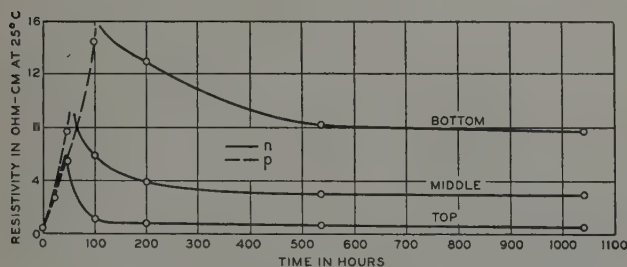


Fig. 6—Effect of heat treatment at 400°C on the resistivity of thermally converted *p*-type germanium from different positions in the ingot.



levels as the temperature of heat treatment is increased.

Two mechanisms for the increase in acceptor concentration have been given, one postulating a change in solubility of an acceptor impurity, the other postulating the formation of acceptor centers by thermally produced lattice defects.

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### Technical Note

## Grain Boundary Effect In Surface Tension Measurement

by Harry Udin

IN 1948, the writer and his associates determined the surface tension of solid copper by balancing the force of surface tension in a very fine wire against an external load.<sup>1</sup> At that time we, in common with other early workers, assumed that grain boundary energy in a pure metal is very small in comparison to the energy of an external surface. Accordingly, we neglected the internal surface energy of the coarse-grained specimens.

Since that time, experimental evidence has accumulated showing that grain boundary energy, far from being small, is generally about one-third of the energy of an external surface.<sup>2-4</sup> This is sufficient to introduce a significant error into our determination. The differential equation governing equilibrium is:

$$w dl = \gamma ds_1 + \gamma^* ds_2 \quad [1]$$

rather than

$$w dl = \gamma ds$$

as originally written.  $w$  is the balancing force in dynes,  $l$  the length of the specimen,  $s_1$  the external and  $s_2$  the internal surface area,  $\gamma$  the copper/copper vapor surface tension, and  $\gamma^*$  the grain boundary tension.

Fortunately, we had made for another purpose a careful study of the size and shape of the grains, and found that the boundaries, with rare exceptions, traversed the specimens and were perpendicular to the wire axis. For this case, eq 1 leads to

$$w = \pi r \gamma - \left( \frac{n}{l} \right) \pi r^2 \gamma^* \quad [2]$$

where  $r$  is the wire radius and  $\left( \frac{n}{l} \right)$  is the number of grains per unit length. A count of some twenty 5-mil wires indicated that  $\frac{n}{l}$  became  $80 \pm 10$  after

a short anneal near the melting point, and remained nearly constant for as long as 96 hr at temperature.

An assumption of  $\gamma^* = 1/3\gamma$  leads to a defining equation for  $\gamma$ :

$$w = \pi r \gamma \left[ 1 - \left( \frac{n}{l} \right) \left( \frac{r}{3} \right) \right] \quad [3]$$

The term in the brackets may be considered a correction factor applied to eq 11 of ref. 1. Upon applying this factor, the surface tension of solid copper at its melting point is found to be  $1650 \pm 100$  dynes per cm, rather than 1370 as previously reported.<sup>1</sup> The new temperature coefficient is  $-0.55$  dynes per cm per °C.

Grain boundary energy is more significant than surface energy to the physical metallurgist. It is evident from eq 2 that a series of experiments with wires of different grain size can lead to an evaluation of  $\gamma^*$ . The details of such an experiment are being worked out now.

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HARRY UDIN is Assistant Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.  
TN 51 E. Manuscript, Nov. 9, 1950.



# Crystallographic Angles For Magnesium, Zinc and Cadmium

by Edward I. Salkovitz

THE determination of the orientation of metal single crystals and the studies of plastic deformation are greatly facilitated by the use of the stereographic projection. To draw a standard projection of the crystal it is necessary to have a tabulation of the angles between the various crystallographic planes of the particular crystal studied. Bozorth<sup>1</sup> has published such a table for the cubic system which can be found in many reference books; such convenient tabulation for the hexagonal metals, however, does not appear to be in the literature, although scores of workers have calculated these angles. Therefore, Table I of angles for magnesium, zinc, and cadmium has been compiled. Since the *c/a*

Table I. Angles Between the Crystallographic Planes in Close-Packed Hexagonal Crystals of Magnesium, Zinc, and Cadmium

| HKIL           | hkil           | Magnesium<br>( <i>c/a</i> = 1.6235) |       | Zinc<br>( <i>c/a</i> = 1.8563) |       | Cadmium<br>( <i>c/a</i> = 1.8859) |       |
|----------------|----------------|-------------------------------------|-------|--------------------------------|-------|-----------------------------------|-------|
| 0001           | 10 $\bar{1}$ 8 | 13°                                 | 11.3' | 15°                            | 0.0'  | 15°                               | 13.6' |
|                | 10 $\bar{1}$ 7 | 14°                                 | 59.6' | 17°                            | 1.5'  | 17°                               | 16.8' |
|                | 10 $\bar{1}$ 6 | 17°                                 | 33.5' | 19°                            | 39.5' | 19°                               | 56.8' |
|                | 10 $\bar{1}$ 5 | 20°                                 | 33.2' | 23°                            | 12.3' | 23°                               | 32.1' |
|                | 10 $\bar{1}$ 4 | 25°                                 | 6.7'  | 28°                            | 10.6' | 28°                               | 33.8' |
|                | 20 $\bar{2}$ 7 | 28°                                 | 10.5' | 31°                            | 29.0' | 31°                               | 53.3' |
|                | 10 $\bar{1}$ 3 | 32°                                 | 0.1'  | 35°                            | 32.7' | 35°                               | 58.5' |
|                | 20 $\bar{2}$ 5 | 36°                                 | 51.1' | 41°                            | 24.6' | 41°                               | 3.4'  |
|                | 10 $\bar{1}$ 2 | 43°                                 | 8.9'  | 46°                            | 59.0' | 47°                               | 26.1' |
|                | 20 $\bar{2}$ 3 | 51°                                 | 20.0' | 55°                            | 1.0'  | 56°                               | 12.8' |
|                | 10 $\bar{1}$ 1 | 61°                                 | 55.6' | 64°                            | 59.5' | 65°                               | 20.1' |
|                | 20 $\bar{2}$ 1 | 75°                                 | 4.0'  | 76°                            | 52.2' | 77°                               | 4.1'  |
|                | 10 $\bar{1}$ 0 | 90°                                 | 0.0'  | 90°                            | 0.0'  | 90°                               | 0.0'  |
|                | 21 $\bar{1}$ 2 | 68°                                 | 2.4'  | 70°                            | 37.1' | 70°                               | 51.4' |
|                | 21 $\bar{1}$ 1 | 78°                                 | 36.9' | 79°                            | 59.8' | 80°                               | 9.2'  |
|                | 21 $\bar{1}$ 0 | 90°                                 | 0.0'  | 90°                            | 0.0'  | 90°                               | 0.0'  |
|                | 11 $\bar{2}$ 8 | 22°                                 | 5.3'  | 24°                            | 53.7' | 25°                               | 14.5' |
|                | 11 $\bar{2}$ 6 | 28°                                 | 25.3' | 31°                            | 44.9' | 32°                               | 9.3'  |
|                | 11 $\bar{2}$ 4 | 39°                                 | 4.2'  | 42°                            | 51.7' | 43°                               | 19.1' |
|                | 11 $\bar{2}$ 2 | 58°                                 | 22.2' | 61°                            | 41.3' | 62°                               | 3.9'  |
|                | 11 $\bar{2}$ 0 | 90°                                 | 0.0'  | 90°                            | 0.0'  | 90°                               | 0.0'  |
| 10 $\bar{1}$ 0 | 12 $\bar{3}$ 2 | 68°                                 | 2.4'  | 70°                            | 37.1' | 70°                               | 51.4' |
|                | 12 $\bar{3}$ 1 | 78°                                 | 36.1' | 79°                            | 59.6' | 80°                               | 9.2'  |
|                | 12 $\bar{3}$ 0 | 90°                                 | 0.0'  | 90°                            | 0.0'  | 90°                               | 0.0'  |
|                | 0 $\bar{1}$ 10 | 60°                                 | 0.0'  | 60°                            | 0.0'  | 60°                               | 0.0'  |

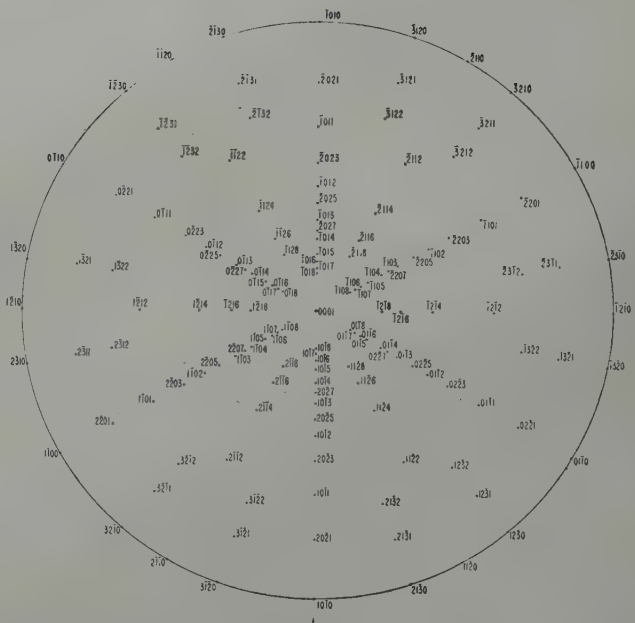


Fig. 1—Standard (0001) projection for zinc hexagonal *c/a*=1.856.

ratio is different for each of these metals, three separate calculations are necessary.

The angles  $\phi$  between (*HKIL*) and (*hkil*) were calculated by means of the formula:

$$\cos \phi = \frac{Hh + Kk + \frac{1}{2}(Hk + hK) + \frac{3}{4} \frac{a^2}{c^2} Ll}{[(H^2 + K^2 + HK + \frac{3}{4} \frac{a^2}{c^2} L^2)(h^2 + k^2 + hk + \frac{3}{4} \frac{a^2}{c^2} l^2)]^{1/2}}$$

The *c/a* ratios were calculated from data given in the 1948 edition of Metals Handbook. Fig. 1 is a typical (0001) standard projection of zinc. For all practical purposes, it serves for cadmium as well, as can be seen from the table. For magnesium, however, it is necessary to construct another net.

<sup>1</sup> R. M. Bozorth: *Physical Review*. (1925) 26, 390.

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TN 50 E. Manuscript, Oct. 10, 1950. Part of these calculations were made at Carnegie Institute of Technology.



# Observations on Rimming Steel Ingots

by A. Hultgren, G. Phragmen, S. Wohlfahrt and J. E. Ostberg

Detailed study was made of a number of rimming ingots, both low and high carbon, and especially upon effects of superimposed air pressure. Requirement to suppress core bubbles is between 10 and 15 atm; at 6.5 atm freezing was in semikilled manner and at 3 atm, steel was of rising type. Probable mechanism of freezing under various conditions is discussed.

AN earlier paper<sup>1</sup> reported an investigation made by a committee for studying rimming steel ingots appointed by Jernkontorets in Stockholm. The present paper is the outcome of some further work done by the same committee.

Since the characteristics of ordinary rimming steel are connected closely with the amount of gas liberated during freezing and since this amount of gas is governed by the pressure, it was considered of interest to ascertain in what manner and to what extent definite pressures applied to the top of the liquid steel in the mold would affect the solidification process and the consequent structure of a rimming steel of ordinary composition.

The experiments were made at the Domnarfvet Steel Works. The steel was made according to normal practice in a 4-ton Rennerfelt electric furnace. Ferromanganese was added in the furnace; no aluminum was added, with one exception. Analyses of the four heats are given in Table I.

The top-poured ingots measured about 12 in. sq x 48 in. and weighed about 1300 lb. One or two ingots of each heat were allowed to solidify under pressure, using a special device for admitting compressed air to the upper closed part of the mold, as shown in Fig. 1. A heavy plate sealed with asbestos was bolted to the top of the mold. The plate had a tapered aperture for pouring. Immediately after pouring the hole was closed by a wedged plug, and compressed air was admitted through a hole in the plug. Because of some delay in applying the plug, full pressure was not reached immediately. The pressure was adjusted to the desired value as indicated by a manometer. In order that the interior of the

ingot might have the benefit of the pressure, the freezing of the top crust was delayed by a refractory lining applied to the top part of the mold, Fig. 1. Ingots were also cast from each heat without applied pressure, and with and without refractory lining at the top.

Axial sections of ingots were cut either of the whole ingot or of some part of it of special interest; sections were polished and usually etched.<sup>1</sup>

To facilitate description of structures the following terms may be used for different types of ingots solidified under gas evolution:

1. *Box-hat or boot-leg ingot*: Abundant gas evolution during casting and during rimming; no rim holes.
2. *Normal rimming ingot*: Lively gas evolution during rimming; usually rim holes in lowest part of

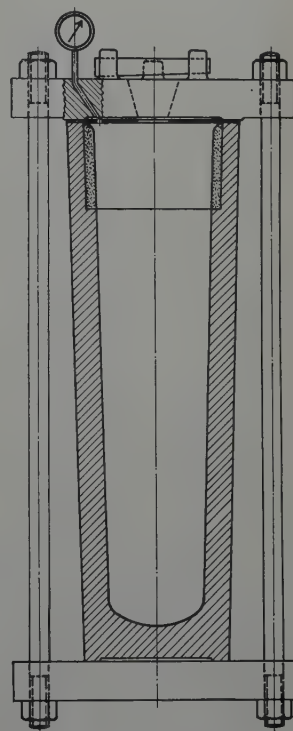


Fig. 1—This test mold shows the arrangement for freezing under pressure. To insure the benefit of pressure to the interior of the ingot, freezing of the top crust is delayed by a refractory lining at the top of the mold.

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This paper is a somewhat revised translation of a report that appeared in Swedish in "Jernkontorets Annaler" (1950).



Fig. 2 (below)—Section of Ingot 7521-5. Without lines and no pressure.

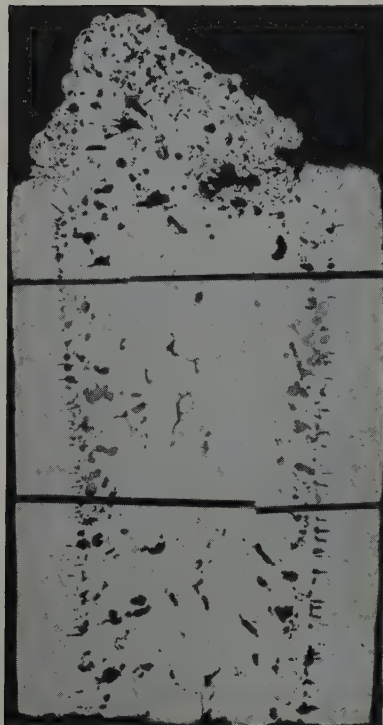


Fig. 3 (right)—Sections of Ingot 7521-3. With lines and no pressure.

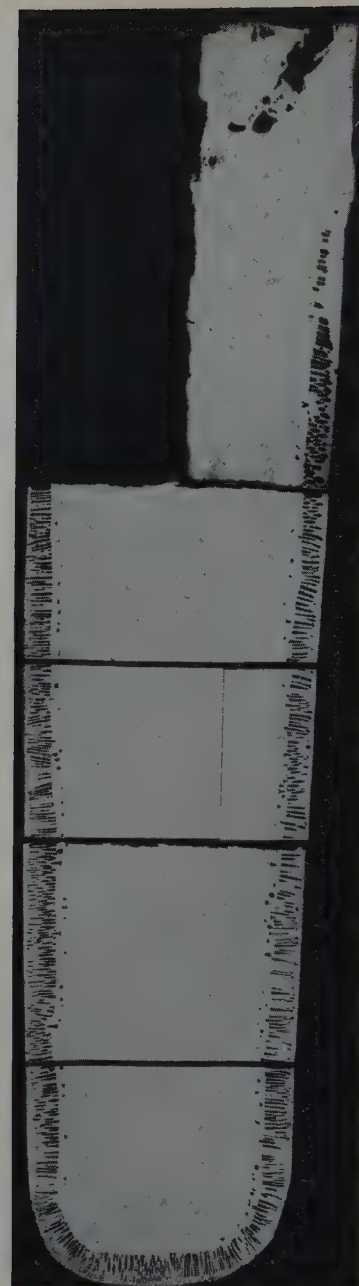


Fig. 4—Distribution of blow-holes in Ingot 7521-4. Applied pressure upon completion of casting was 15 atm.

ingot, the volume of which roughly balances shrinkage during solidification of rim zone, with the result that the top surface retains about the same level during rimming.

3. *Rising ingot*: Moderate gas evolution during rimming period causing rim holes to form along more than half the ingot, their total volume exceeding shrinkage in this period and thus causing the top surface to rise continuously.

4. *Semikilled ingot*: Slight gas evolution; the gas evolved remains wholly or largely as blowholes, usually oblong and located in upper half of ingot, where ferrostatic pressure is low enough for gas

Table I. Composition of Test Heats

| Heat   | Composition, Pct |                 |      |       |       |
|--------|------------------|-----------------|------|-------|-------|
|        | C                |                 | Mn   | P     | S     |
|        | Killed Sample    | Unkilled Sample |      |       |       |
| J 7338 | 0.06             |                 | 0.32 | 0.009 | 0.024 |
| J 7521 | 0.12             |                 | 0.48 | 0.013 | 0.027 |
| J 7646 | 0.08             |                 | 0.33 | 0.008 | 0.015 |
| J 7699 | 0.07             | 0.10            | 0.24 | 0.010 | 0.028 |





Fig. 5 (left)—Etched section of top of Ingot 7521-4, not heat treated.

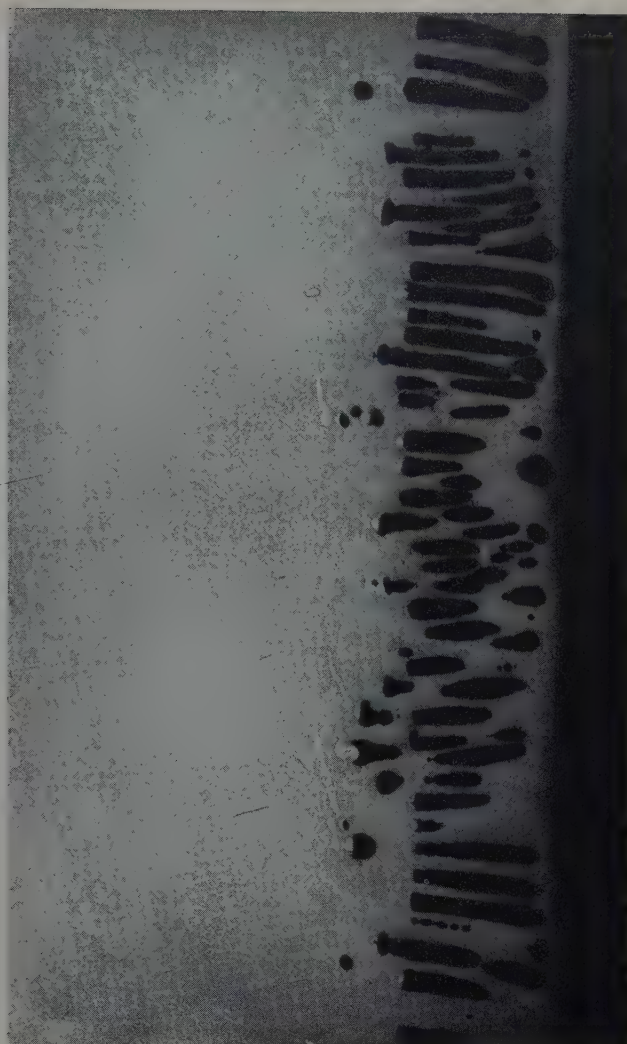


Fig. 6 (right)—Etched section of a heat-treated section of the middle portion of Ingot 7521-4.

liberation; when blowhole volume balances shrinkage no pipe cavity is formed.

### Results

*Heat J 7521: Ingot 7521-5, No pressure applied, no refractory top lining, Fig. 2:* Only the top 18 in. was sectioned. Rim holes are absent, which is normal. Rim channels are present after passing into small blowholes at the inner end. There is a large cauliflower or nigger head at the top.

*Heat J 7521: Ingot 7521-3, No pressure applied, refractory top lining, Fig. 3:* The structure indicates that the mold was filled to about 4 in. beyond the beginning of the lining. During rimming the level of the steel rose about 4 in. Later, liquid metal penetrated the top crust, forming a cauliflower.

Rim holes terminate only 10 in. below the lining; their length decreasing continuously from the bottom end upward. The inner part of the rim zone bordering on the intermediate blowholes is almost solid, like the uppermost part. The rising top level and the larger total rim-hole volume are obviously connected.

The core contains many blowholes, their volume being related to the volume of liquid steel that escaped through the top crust. In the lower third of the core, the core holes form pointed V patterns, to be explained as follows: After this part had reached a late stage of solidification and had developed numerous large blowholes, solidification proceeded further toward the top under pressure, causing the still deformable bottom aggregate to give way, its blowholes being compressed.

A few large vertical blowholes are also seen along the axis in the lower part. Their volume equals the

sum of the shrinkage and the compression of the surrounding blowholes during the final freezing period. These central blowholes seem not to have been compressed, probably because the stiff metal aggregate at this late stage resists the higher pressure from above.

The gas pressure of a freezing steel is a function of the composition of the mother liquor from which gas is evolved. The cause of the vertical pressure gradient postulated probably was the fact that, through sedimentation of suspended crystals, the lower portion of the core at a given temperature during freezing contained less mother liquor than the upper portion and, in consequence, its final degree of segregation was less.

The fact that this ingot rose during rimming indicates that less gas was evolved in unit time than in ingot 7521-5 during this period, possibly because of retardation of freezing by the top lining.

*Heat J 7521: Ingot 7521-4, applied pressure, 15 atm:* Full pressure was reached 1 min-22 sec after the end of casting. Fig. 4 shows the distribution of blowholes and Fig. 5 the etched section of half the top portion, by oversight not annealed.\* A columnar structure is faintly visible in the etched surface. This is not the primary structure but the austenite structure formed during cooling. (The true primary structure of a section taken about half height is seen in

\* Usually, in order to obliterate the traces of secondary ( $\gamma$  transformation) structure, the sections were heat treated by heating to about 1000°C, water quenching, and tempering several hours at 700°C.





Fig. 7—Section of the top of Ingot 7521-2, not heat treated. Columnar secondary structure was observable in the original. Applied pressure was 10 atm.

Fig. 6; this section was heat treated.) In Fig. 5 is seen a lower set of wide rim holes beginning near the surface and ending about 1 in. beneath it.

These rim-holes had begun to form before pressure was applied and afterwards continued to grow until the total pressure reached was sufficient to suppress gas evolution. Farther upward a short set of blowholes appears beginning about 0.6 in. beneath the surface. The solid 0.6 in. surface layer is of the type common in the upper part of rimmed ingots; it indicates ample gas evolution. With the exception of the blowholes described, the ingot section is solid up to the funnel-shaped porous region at the top, Figs. 4 and 5, probably formed by the top crust, as shrinkage proceeded, being forced downward like a cork in a bottle.

The primary structure displayed in Fig. 6 enables a detailed study of the mode of freezing. The rim holes show the well-known alternate constrictions and expansions. Their inner end is flattened and terminated by a "segregation button." Each blowhole temporarily reached farther inward and, owing to the rising pressure, a portion of a partly frozen mass was pressed into it and some mother liquor was squeezed out, forming the button.

In a zone farther inward, occasional extensions of rim holes occur as well as separate rounded blowholes, without visible connection with the rim holes. The latter also are flattened at their inner ends and have a button segregate. In addition, a steeply

sloping string of segregate is often attached to such a blowhole. The latter blowholes probably formed under rising pressure in the following way: During the rimming period a great many gas bubbles detach and rise. By the resulting rapid upward movement of the liquid metal, the mother liquor at the solidification front is largely removed and mixed with the main mass of the liquid. In other words, the liquid metal into which the crystals grow is relatively little segregated. As the pressure rises, gas evolution stops, hence movement of the liquid also. During subsequent freezing in quiet liquid two simultaneous changes occur: (1) pressure rises continuously, and (2) the mother liquor at the front is rapidly enriched in alloying elements, including carbon and oxygen. Gas evolution is suppressed by 1 and promoted by 2. When the effect of 1 predominates the growth of the rim holes is stopped; their inner ends are compressed; and depressions form in the solidification front opposite the blowholes. If, however, 2 overtakes 1, owing to the slow rise of pressure, new blowholes appear, preferably in the depressions where enrichment is greater. If such blowholes are openly spaced and if they expand faster inward than the front grows, their inner ends lack support; hence they detach themselves and rise. Since, at this stage, the surrounding mass probably contains crystals, the bubble will rise slowly, displacing crystals which do not close up behind the bubble. The mother liquor in the wake of the rising bubble forms string segregate. Such steep string segregates were observed earlier in steel ingots insufficiently killed. Their absence in ordinary rimming-steel ingots is probably caused by the fact that

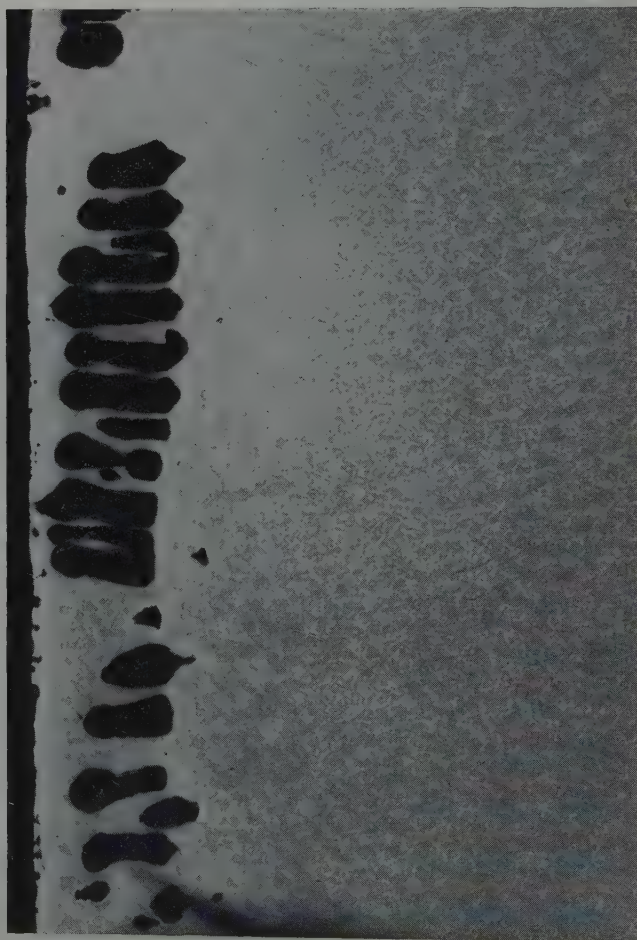


Fig. 8—Reverse side of section shown in Fig. 7 in the annealed condition.



rimming and movement in the liquid goes on to the stage at which the moving mass is sluggish enough to prevent the bubbles from rising.

*Heat J 7521: Ingot 7521-2, applied pressure, 10 atm: Full pressure was reached 2 min-3 sec after casting was finished.*

Fig. 7 shows the columnar secondary structure of the ingot top, not heat treated. The rim holes end 14 in. below the top insulation, consequently this ingot showed, like ingot 7521-4, greater rising tendency during rimming than ingot 7521-3, solidified without applied pressure in a mold with refractory top lining. Presumably the cap applied to the mold to some extent obstructed the reaction of the steel with the oxygen of the air, thus restricting gas evolution during rimming.

The central top area is more porous than in ingot 7521-4 (15 atm), a natural consequence of the lower applied pressure (10 atm); otherwise the interior of this ingot also is solid.

The rim holes end at a depth of about 0.6 in. beneath the ingot surface. Fig. 8 (annealed, back of section shown in Fig. 7) shows a fine dendritic primary structure extending to about 1 in. from the surface. The inner ends of the rim holes are flat or have a blunt shape. In the intermediate region farther inward are outlined extensions of the holes which have been filled and also freshly formed blowholes largely filled with a mass of coarser primary structure with continuous transition into the core structure. Up to about 3.5 in. from the surface, the core shows random dendritic patches; farther in the structure it is wholly globular. The dendritic intermediate zone indicates a scarcity of crystal nuclei in the liquid at the stage at which the rising pressure stopped gas evolution. The fact that the rim holes of this ingot are shorter than those of ingot 7521-4 is unexpected in view of the longer time for reaching full pressure.

*Heat J 7699: Ingot 7699-A, applied pressure, 6.5 atm: Full pressure was reached after 57 sec.*

Fig. 9 shows the blowhole distribution in the ingot. The external zone up to about 0.8 in., is free from blowholes but contains numerous rim channels; hence, there was more gas evolution in the early stage of freezing than in heat 7521. Inside this external zone, an intermediate zone extending to about 2 in. from the surface, shows numerous narrow blowholes, often interrupted. These were formed under rising pressure. The lower part of the core is practically solid but in the upper part are seen long narrow blowholes converging toward the center of freezing, typical of a semikilled steel ingot. In the middle portion along the axis, a set of fine cores is seen.

Freezing probably proceeded as follows: When the pressure was applied the top level sank about 8 in. The pressure was, however, insufficient for complete suppression of gas evolution. On continued freezing, therefore, the blowholes formed caused the top level to rise about 3.5 in. in 2 to 3 min. After full pressure was attained the top surface was frozen over, as judged from the thickness of the crust. At this moment the core material probably consisted of a great quantity of crystals and little mother liquor. For this reason the final stage of freezing was associated with a small amount of shrinkage and, in consequence, only small cores and few blowholes were formed. In the bottom portion, radial as well as vertical blowholes occur. The latter type of holes was seen also in ingot 7646-4 (below).



Fig. 9 (above)—Sections of Ingot 7699-A, which was solidified under pressure of 6.5 atm.

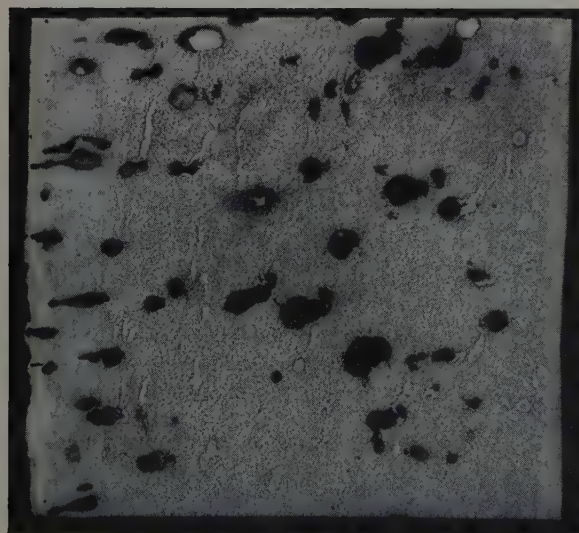
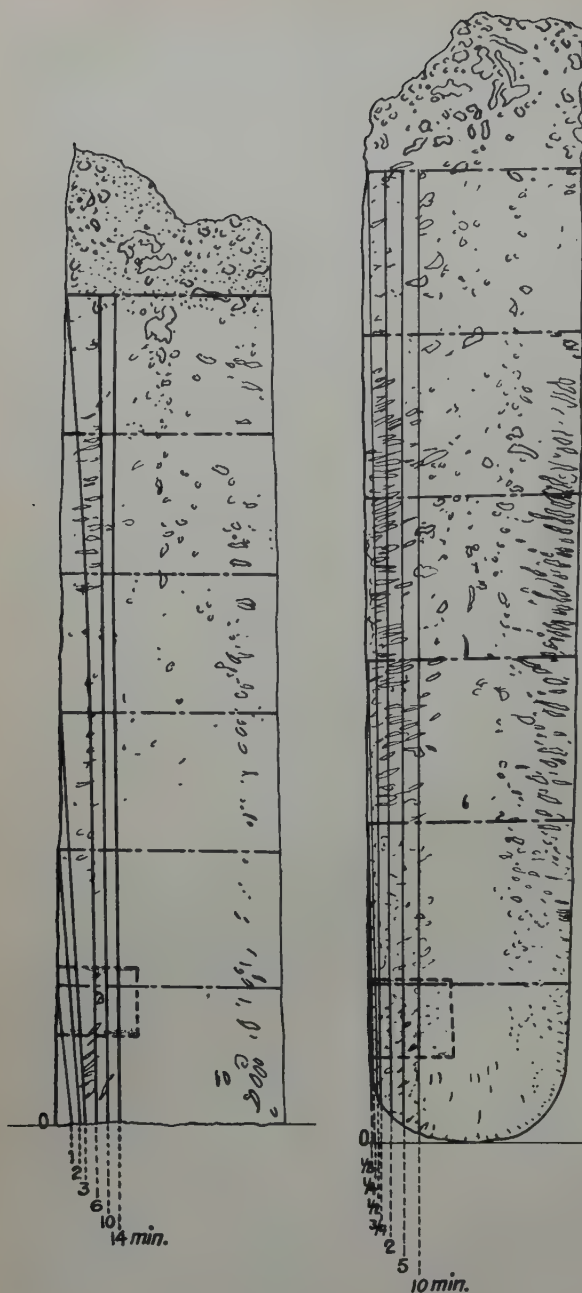
Fig. 10 (right)—Sections of Ingot 7646-4, which was solidified under a pressure of 3 to 4 atm.

*Heat J 7646: Ingot 7646-4, applied pressure varying between 3 and 4 atm: About 2 oz per ton of aluminum was added to the ladle. Full pressure was reached 50 sec after end of casting.*

Fig. 10 shows the blowhole distributions in the ingot. Freezing probably occurred as follows: Before pressure was applied, rim holes formed in the lower part of the ingot (blowhole zone I) reaching a maximum depth of 1 in. near the bottom. From the bottom toward half height the length of the rim holes gradually decreased to zero, their outer boundary moving inward and their inner boundary moving outward; the upper half of the rim zone is correspondingly nearly solid.

In the lower third of the ingot, blowhole zone I is succeeded by a solid intermediate zone about 0.4 in. thick, indicating that the sum of applied and ferrostatic pressures in this portion was sufficient for suppression of gas evolution at this degree of segregation.





Proceeding inward, the next zone is characterized by numerous long blowholes in a direction deviating somewhat in an upward direction from the perpendicular to the surface (blowhole zone II). It is assumed that, through segregation, the mother liquor has passed the composition corresponding to gas saturation at the established total pressure. These blowholes are not regarded, therefore, as rim holes. In the upper half of the ingot the solid rim zone is followed directly by blowhole zone II. This zone is followed by a solid core of about one third the ingot width. At the boundary the blowholes are often flattened or bent upwards. Along the axis and in the top part some porosity may be seen.

The great volume of the blowholes in zone II has its counterpart in a top portion formed by rising during this stage of freezing, to the extent of 6.3 in. beyond the original level before the cap stopped it. The moment of capping then corresponds to cessation of blowhole formation.

In the bottom portion, and occasionally in upper portions also, roughly vertical, long blowholes and rows of such holes are found, mostly in zone II, but a few in the core also. Probably there has been enough gas evolution for the inner ends of some of the perpendicular blowholes to detach themselves ahead of the actual freezing front and to rise slowly, their movement being retarded by the sluggish consistency of the aggregate. In other words, the perpendicular growth of a blowhole indicates that it is adequately supported by the surrounding solidified steel. The fact that the rising gas bubbles were retained as blowholes and did not move to the top is, of course, a sign of a sluggish mass. The comparative solidity of the core region also results from the small amount of mother liquor in the aggregate when rising was checked.

Reviewing the results reported above for rimming steel solidified at different pressures, it is seen that under the conditions of the experiments, an applied pressure of 15 atm was sufficient to prevent all gas liberation as bubbles in the core of the ingot, while 10 atm was not quite sufficient. Disregarding the shielding effect of the top crust in later stages of freezing, the final composition of the mother liquor in these ingots seems to correspond to an applied pressure of 10 to 15 atm. It is of course possible that some supersaturation is required before gas is liberated, in which case the equilibrium pressure was still higher. Rimming steel subjected to such pressures behaves, of course, like a killed steel during freezing. At an applied pressure of 6.5 atm, the steel froze like a semikilled steel, and at 3 atm like a rising steel.

#### Rimming Steel with High Carbon Content

Since rimming steel with about 0.40 pct C is used to some extent in Sweden, three ingots of such material were examined, two made at Degerfors and one at the Surahammar works.

*Ingots Made in Degerfors:* One top and one bottom poured ingot were available from different basic open-hearth heats; compositions are given in Table II. The compositions were similar, with the exception of phosphorus which was considerably higher in the first ingot. Casting time was about 45 sec for the

Fig. 11 (top left)—Blowhole distribution in high-carbon ingots, bottom and top poured, respectively, computed freezing-front positions are shown also.  
a—left. b—right.

Fig. 12 (bottom left)—Section of the top-poured ingot at location indicated in Fig. 11b.



Table II. Composition of High-Carbon Ingots

| Heat   | Composition, Pct |    |      |       |       | Casting Method |
|--------|------------------|----|------|-------|-------|----------------|
|        | C                | Si | Mn   | P     | S     |                |
| M 3110 | 0.40             |    | 0.58 | 0.061 | 0.039 | top-poured     |
| M 3090 | 0.37             |    | 0.58 | 0.014 | 0.037 | bottom-poured  |

top-poured, and about 6 min for the bottom-poured ingot.

Blowhole distribution in both ingots is shown in Fig. 11, which also gives freezing front positions for a series of intervals after casting commenced. These positions were calculated from the formula  $D = 0.87\sqrt{t}$ , where  $D$  is thickness in in., and  $t$  time in min. The top-poured ingot has more blowholes in the rim zone than has the bottom-poured one. Both show cauliflower tops.

Fig. 12 shows the primary structure of a selected part of the section of the top-poured ingot, its position being indicated in Fig. 11. Corresponding freezing front lines are plotted in Fig. 13. The skin portion (zone I), about 0.15 in. thick, shows numerous "blowhole seats" too small to be visible in reproduction. Next inward is zone II, extending to a depth of about 0.6 in., showing dendritic structure and containing some large blowholes but no blowhole seats. The next zone, III, also contains blowholes but has a globular primary structure. A reconstruction of the freezing sequence would be as follows: Zone I obviously is solid as a result of strong gas evolution, most bubbles being scrubbed off, leaving blowhole seats. Zone II formed under limited gas evolution—rising type—and zone III formed under increasing gas evolution with most of the gas moving away. Upward passage of the bubbles was retarded by projections in the freezing front and suspended small crystals. In this way the marked steep string segregates were formed. Blowhole segregates formed on compression of blowholes with each new gas bubble forming at a higher pressure than a preceding one nearer the surface.

The successive formation of three distinct zones can be explained if the variation in ferrostatic pressure during the rapid casting is considered. While zone I froze, the pressure was low and gas evolved freely. As the steel level rose and pressure with it, less and less gas was liberated (zone II). After casting was finished, and under the following period of stationary ferrostatic pressure, gas evolution increased as segregation mounted. This explanation appears to agree with the position of the freezing front lines plotted in Fig. 13.

Most of the oblong blowholes in the rim zone of this ingot, consequently, are believed to be of the kind typical of rising steel. In the top fifth of the ingot—below the top part that has risen—there are only a few blowholes in the rim zone, probably owing to a lower ferrostatic pressure and hence greater gas evolution.

A similar selected part of the bottom-cast ingot is shown in Figs. 14 and 15. Here also three zones may be distinguished. On account of the slow casting—6 min—zone I, with numerous blowhole seats, disturbed dendritic structure, and few blowholes indicating strong gas evolution, is about 1 in. thick. Its inner boundary may be calculated to correspond with a moment  $2\frac{1}{2}$  min after casting commenced and with a steel level almost half way up. Zone II extends to about 2.5 in. from the surface corresponding to 8 min after zero casting time. During this period, the ferrostatic pressure was sufficient to

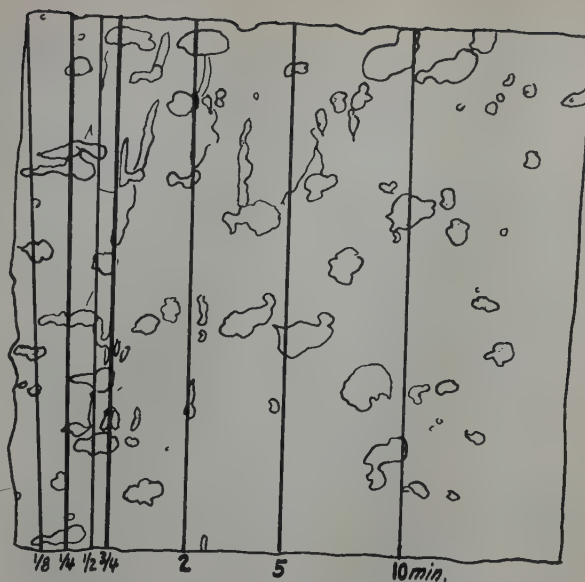


Fig. 13—Freezing-front lines for section shown in Fig. 12.

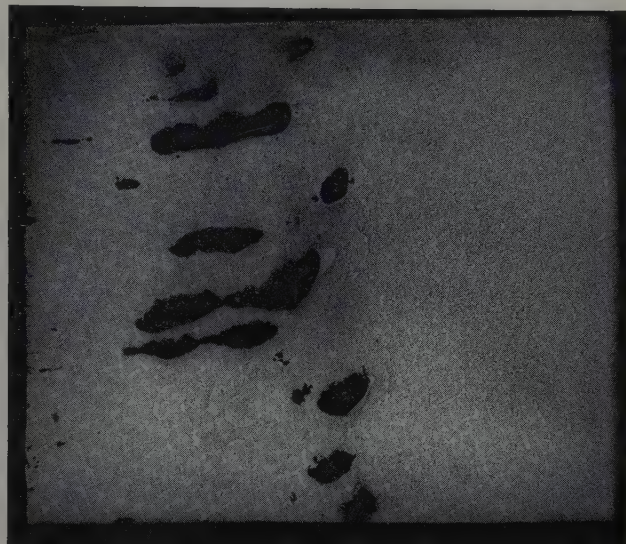


Fig. 14—Section of the bottom-poured ingot at location indicated in Fig. 11a.

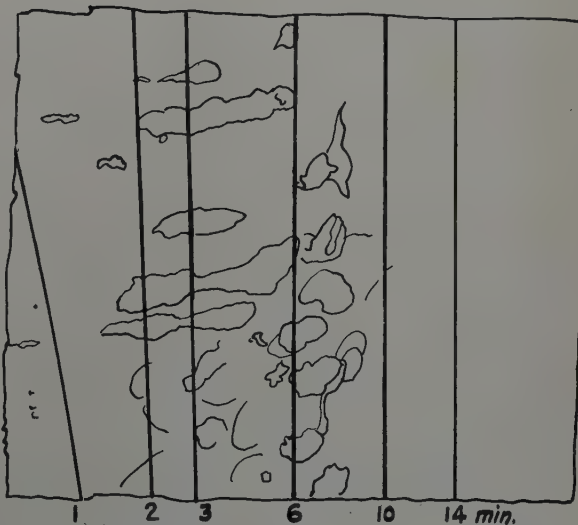


Fig. 15—Freezing front lines for section shown in Fig. 14.



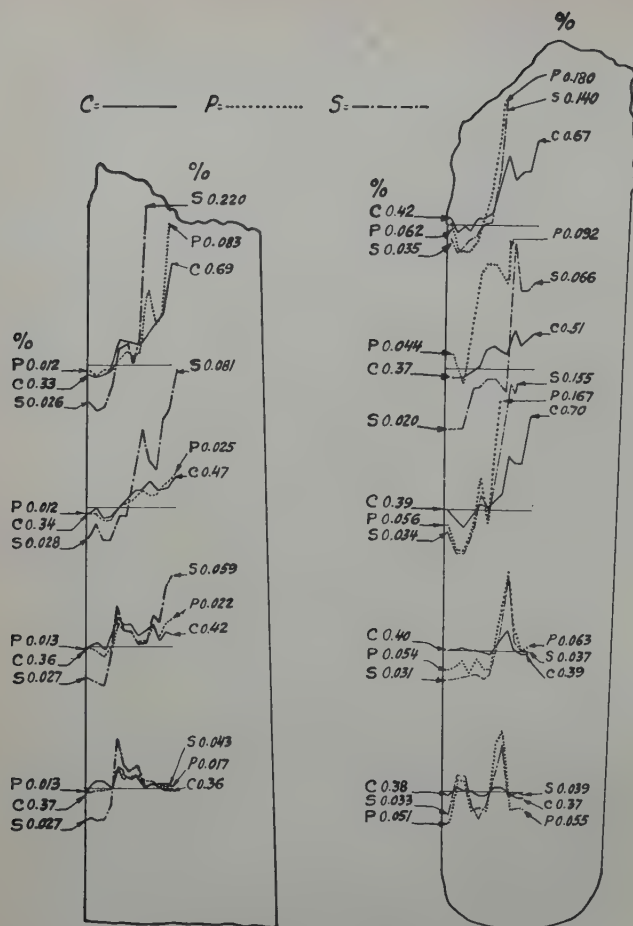


Fig. 16—Carbon, phosphorus, and sulphur variation in the high-carbon ingots.

check gas evolution, to such an extent that part of the gas remained as large blowholes and part came off, leaving large blowhole seats. Reasoning similar to that given for the top-cast ingot applies to zone III. During this period, when the top crust was not yet strong enough, liquid penetrated it and formed a top part above the crust. A considerable volume of blowholes must have formed simultaneously to account for this phenomenon. These holes were later largely compressed when new blowholes formed in the core. In this way the inner boundary of zone III was moved outward.

Analyses of drilled samples taken from different levels in the two ingots are given in Fig. 16. The low values found in the outer part of the rim zone are evidence of strong gas evolution and movement. In the top-cast ingot, the phosphorus and sulphur contents at the lower levels show a maximum within zone II, in agreement with the postulated checked gas evolution; otherwise, the distribution of elements is similar in the two ingots. As a result of sedimentation segregation, the core shows low values in the bottom portion, and high values in the top portion. Certain peaks within the core are probably due to blowhole segregates.

*Ingots Made in Surahammar:* One 12 in. top-cast ingot made in the acid open-hearth furnace was examined. It contained: 0.38 pct C, 0.03 pct Si, 0.46 pct Mn, 0.34 pct P, and 0.018 pct S. Ferromanganese was added in the furnace, but no aluminum. Casting lasted less than 1 min. Gas evolution was uniform and top level did not change during rimming. Eight to ten minutes after casting the ingot was capped. The rim was then 4 in. wide.

Fig. 17 shows the blowhole distribution. Some large rim holes appear in the lower half of the ingot and in its top portion. In the region where rim holes are absent there are intermediate blowholes. The core is solid, except for a few large blowholes around and at the freezing center in the top.

The primary structure of a section from half height is seen in Fig. 18. Surface zone I, about 1 in. thick, corresponding with a time of formation of 1.3 min, contains few blowholes and has a disturbed finely dendritic structure with occasional blowhole seats. Obviously it froze under fairly strong gas evolution. Next is solid zone II, with globular structure and with blowhole seats here and there. It is terminated at a depth of about 2.5 in. by some intermediate blowholes. This depth seems to correspond to the moment of capping. The transition to the core zone with its globular structure is otherwise smooth.

This ingot is somewhat more solid than the two already described of a similar composition, indicating good rimming action. Possibly the casting temperature was low, whereby freezing was accelerated

Fig. 17 (right) — Blowhole distribution in a high-carbon acid open-hearth ingot.





and the amount of gas liberated per unit time was greater. Why rim holes formed in the upper part where gas evolution and movement during rimming should have been strong is not clear.

The high-carbon rimming steel ingots examined differ in some respects from rimming steel ingots with 0.055 to 0.21 pct C examined earlier.<sup>1</sup> Increasing carbon content increases the development by etching of primary dendritic structure in the surface zone. Further, there is, in the high-carbon ingots, a tendency for a globular structure to develop fairly early during the formation of the rim zone. Gas bubbles appear to detach themselves less easily and, during rising, are more often detained than in lower carbon ingots. To some extent, the lesser amount of gas set free may be responsible. On the other hand, the widening of the freezing range caused by the higher carbon content may be of importance. The degree of segregation with respect to the distribution of phosphorus, sulphur, etc., between solid and liquid probably increases with the carbon content; thus, the marked contrast in the etched structure is explained. Further, the depth of the freezing zone during growth of the rim zone is increased for the same reason; in other words, the freezing front is less smooth, with the effect on the bubbles referred to. The uneven front should also tend to retard the movement of the liquid.

Globular primary structure indicates the presence of numerous small crystals in the liquid. Possibly protruding points of the crystals growing from the wall are to some extent broken off by the moving liquid. The main cause of the globular structure, however, is believed to be connected with the stronger segregation in the liquid steel ahead of the freezing front and the consequent retardation of the growth of the rim zone. The temperature of this segregated liquid corresponds to its liquidus and is therefore lower than the liquidus for the main melt immediately inside it which is only slightly contaminated by mother liquor. Thus the latter will be subjected to turbulence below its liquidus temperature; in other words, the conditions for precipitation of numerous crystals and formation of a globular, nondendritic structure are realized. High contents of other elements lowering the freezing point may be assumed to have a similar effect.

The Degerfors steel showed a rising tendency. As ingot M3090 shows, slow casting is likely to counteract this tendency and to produce a fairly thick solid surface zone otherwise typical of normal rimming steel. As stated, the Surahammar ingot had a fairly solid surface zone, despite rapid casting. It may be concluded therefore that a carbon content of 0.40 pct does not preclude good rimming.

### Large Inclusions in Rimming Steel Ingot

In rimming steel ingots large round or rounded nonmetallic inclusions are commonly present. Although their matrix is transparent they usually contain particles of opaque (Fe, Mn)O and MnS or FeS. The matrix, obviously, is a silicate poor in silica. Such inclusions may be seen with a binocular microscope at a magnification of 20 to 30 diam. Their color may be yellowish, brownish, or gray. Some ingots from the earlier investigation<sup>1</sup> were examined in this way; all inclusions above 0.05 mm being measured and counted, and their distribution in the ingot section determined. The results are given in Tables III and IV.

The results may be summarized as follows:

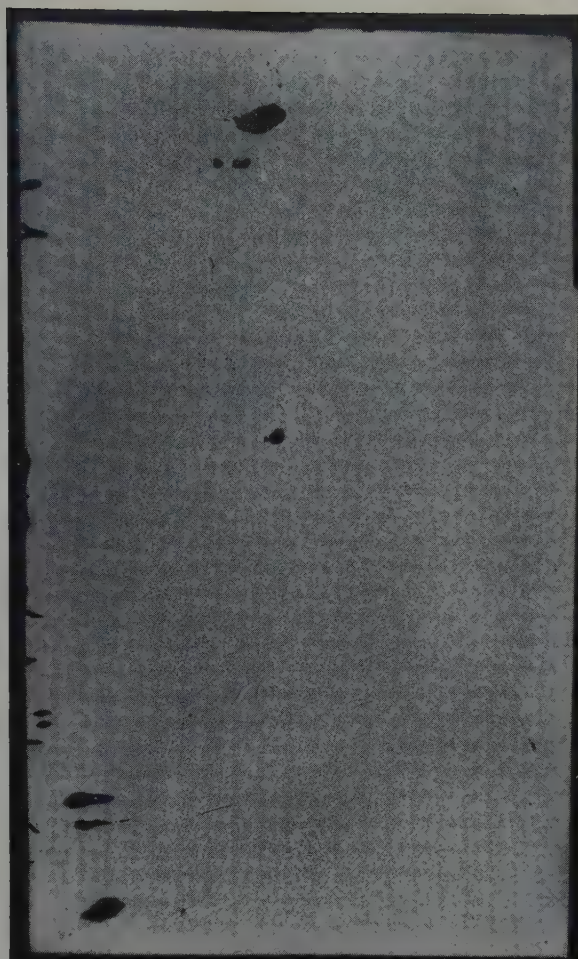


Fig. 18—Structure of a half-height section of the ingot shown in Fig. 17.

1. The core contains a greater amount of large inclusions than the rim zone.
2. In the rim zone, the amount possibly increases towards the bottom.
3. In the core there is a definite such tendency.
4. The amount is not necessarily governed by the carbon content of the steel.

The fact that there are more large inclusions in the core than in the rim zone, although the former, for the carbon contents in question, has a lower oxygen content, probably results from its coarser primary structure in the sense of more open spacing of the small scale segregates. The number of inclusions of the same kind smaller than 0.05 mm would accordingly be less in the core. The accumulation of large inclusions in the lower portion of the core is probably connected with the sedimentation of the metal crystals, a well-known feature in killed-steel ingots also.

### Extent of Continuity in Rim Channels

In an ingot of normal rimming steel, at least the upper half, the rim zone is free from rim holes; however this portion probably always contains long narrow, roughly horizontal pores; so-called rim channels. These, like the rim holes, are assumed to be remnants of gas bubbles evolved at the freezing front during rimming. The movement of the liquid metal in the upper part of the ingot being very rapid, only small portions of the bubbles manage to remain as holes.<sup>1</sup> It appeared to be of interest to establish the extent of continuity existing within each channel.

This was done by cutting sections from a 2-ton



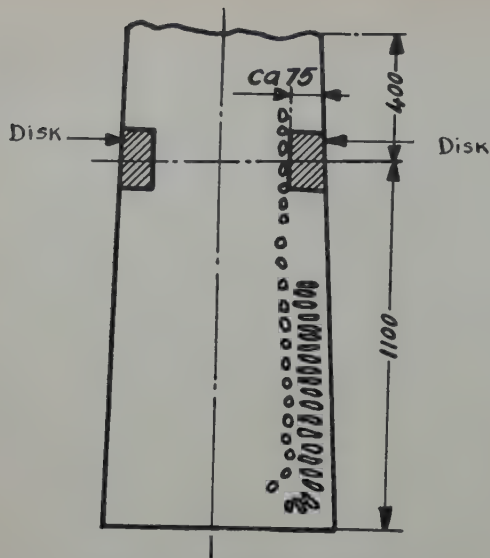


Fig. 19—Location of test samples. Dimensions are in mm.

ingot made at Domnarfvet, containing 0.08 pct C, 0.20 pct Mn, 0.017 pct P, and 0.029 pct S; their locations are shown in Fig. 19. The outer surface was machined to a depth of 0.28 in., corresponding to several times the depth ordinarily lost by burning during heating. The samples were prepared further by installation of a threaded cap, as shown in Fig. 20. Tests were conducted by filling the top depression with water, then putting the space between cap and sample under 8-atm air pressure. Metal was then bored out and the test repeated until the test piece was no longer pressure tight. Boring was done from outside in, in one instance, and inside out in the other. In the first instance, the sample remained pressure tight for a distance from the outside surface of 1¼ in., whereas in boring from the inside surface, a depth of 2⅞ in. was reached before there was leakage. It may be concluded, therefore, that the rim channels were discontinuous to a depth of 1¼ in. from the surface, whereas there was continuity from this depth to the intermediate blowhole zone. Similar results were obtained on samples from a 0.25 pct C ingot.

Table III. Inclusion Distribution in Bottom-Cast Ingots Made at Kallinge

| Sample No. | Average Distance from Bottom, In. | Ingot A, 0.08 Pct C, Vol Pct x 10 <sup>3</sup> |      | Ingot B, 0.09 Pct C, Vol Pct x 10 <sup>3</sup> |      |
|------------|-----------------------------------|------------------------------------------------|------|------------------------------------------------|------|
|            |                                   | Rim Zone                                       | Core | Rim Zone                                       | Core |
| 11         | 34.5                              | 1.1                                            | 1.3  | 0.6                                            | 1.8  |
| 10         | 31.5                              | 0.5                                            | 1.0  | 0.3                                            | 1.8  |
| 5          | 14.7                              | 1.3                                            | 1.0  | 1.7                                            | 1.4  |
| 4          | 11.1                              | 0.7                                            | 2.8  | 3.4                                            | 5.1  |
| 3          | 7.9                               | 1.4                                            | 9.0  | 2.0                                            | 4.4  |
| 2          | 4.75                              | 1.4                                            | 8.0  | 2.2                                            | 8.9  |
| 1          | 1.6                               | 0.9                                            | 8.5  | 0.7                                            | 7.7  |
| Avg        |                                   | 1.0                                            | 4.1  | 1.4                                            | 3.8  |

Table IV. Inclusion Distribution in Top-Cast Ingots Made at Nykroppa

| Sample No. | Average Distance from Bottom, In. | Ingot F1, 0.14 Pct C, Vol Pct x 10 <sup>3</sup> |      | Ingot F3, 0.14 Pct C, Vol Pct x 10 <sup>3</sup> |      | Ingot K1, 0.21 Pct C, Vol Pct x 10 <sup>3</sup> |      |
|------------|-----------------------------------|-------------------------------------------------|------|-------------------------------------------------|------|-------------------------------------------------|------|
|            |                                   | Rim Zone                                        | Core | Rim Zone                                        | Core | Rim Zone                                        | Core |
| 8          | 50.0                              | 0.3                                             | 1.1  | 0.5                                             | 0.3  |                                                 |      |
| 7          | 44.0                              | 0.5                                             | 0.5  | 0.2                                             | 0.8  | 4.9                                             | 0.9  |
| 6          | 38.0                              | 0.8                                             | 1.2  | 0.5                                             | 0.9  | 1.9                                             | 2.5  |
| 5          | 32.5                              | 1.8                                             | 2.5  | 0.3                                             | 0.8  | 1.1                                             | 4.7  |
| 4          | 26.6                              | 2.1                                             | 0.8  | 0.5                                             | 3.0  | 1.5                                             | 8.8  |
| 3          | 20.6                              | 2.9                                             | 1.5  | 0.5                                             | 2.2  | 1.0                                             | 8.6  |
| 2          | 14.7                              | 1.5                                             | 2.5  | 2.7                                             | 3.9  | 1.7                                             | 11.8 |
| 1          | 9.1                               | 1.1                                             | 4.6  | 0.4                                             | 7.9  | 1.6                                             | 14.3 |
| Avg.       | 3.0                               | 0.4                                             | 4.0  | 3.3                                             | 24.2 | 1.2                                             | 10.9 |
|            |                                   | 1.3                                             | 1.8  | 1.0                                             | 4.9  | 2.5                                             | 7.2  |

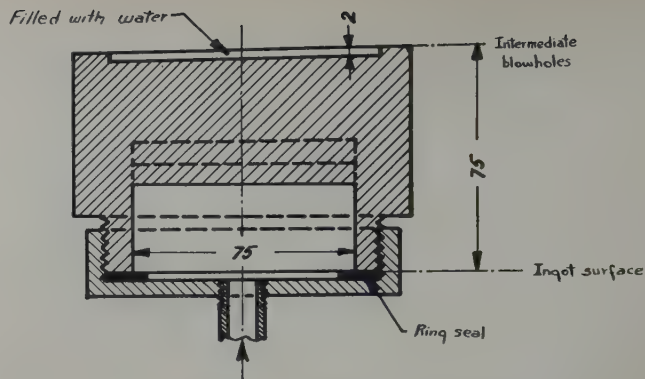


Fig. 20—Details of assembly for continuity test.

### Summary

1. When rimming steel is allowed to solidify under pressure the evolution of gas during solidification is reduced, the more the higher the pressure. Accordingly, blowhole distribution and primary structure are governed by the pressure. When the pressure exceeds a certain minimum, no gas evolution takes place and the structure shows the characteristics of a killed steel.

2. On experimenting with a steel with 0.12 pct C (determined on unkilld sample) and 0.48 pct Mn, an additional air pressure of 10 to 15 atm was sufficient for preventing all gas evolution during solidification. Under an additional pressure of 6.5 atm (0.07 pct C, 0.24 pct Mn) a semikilled ingot was obtained and under 3 to 4 atm (0.08 pct C, 0.33 pct Mn) a rising ingot.

3. The application of a lid, with a casting orifice, appeared to reduce gas evolution during rimming somewhat. Hence the steel may rise during this period. A similar effect probably was produced by a refractory lining at the top of the mold.

4. Rimming steel with about 0.40 pct C differs from such steel of lower carbon contents in that a good rimming action seems more difficult to produce, although not impossible. The inner part of the rim zone tends to develop a globular freezing structure. On slow casting, the outer part of that zone contains fewer blowholes than on rapid casting.

5. Large nonmetallic inclusions in rimming steel ingots with 0.08 to 0.21 pct C appear in larger amount in the core than in the rimming zone and in larger amount in the lower than in the upper part of the core.

6. Rim channels in rimming steel ingots in two cases were found to show continuity from a depth beneath the ingot surface of about 30 mm to the intermediate blowholes but not outside of the 30 mm depth.

The experiments with rimming steel ingots solidified under pressure and the tests to establish the extent of continuity were made at the Domnarfvet Steel Works, the ingots of high-carbon content were made at the Degerfors and the Surahammar steel works. The investigations of structure and inclusions were carried out at the Royal Institute of Technology, Stockholm. For valuable assistance with the latter tasks the authors are indebted to Raymond Nordstrom.

Until his untimely death in 1944, G. Phragmén was very active in the investigations. Behind the results reported stands the whole committee, which since 1940 has included H. Gillo and M. Wiberg.

### References

<sup>1</sup>A. Hultgren and G. Phragmén: Solidification of Rimming-steel Ingots. *Trans. AIME* (1939) 135, p. 133.



# Vanadium-Oxygen Equilibrium in Liquid Iron

by John Chipman and Minu N. Dastur

This paper presents equilibrium data on the reaction of water vapor with vanadium dissolved in liquid iron at 1600°C. The thermodynamic behavior of vanadium and oxygen when present together in the melt is discussed. A deoxidation diagram is presented which shows the concentrations and activities of vanadium and oxygen in equilibrium with  $V_2O_3$  or  $FeV_2O_4$ .

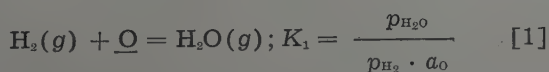
**S**TUDIES of the chemical behavior of oxygen dissolved in pure liquid iron<sup>1-3</sup> have served to determine with a fair degree of accuracy the thermodynamic properties of this binary solution. The practical problems of steelmaking, however, involve not the simple binary but ternary and more complex solutions. Only a beginning has been made toward understanding the behavior of such systems. The silicon-manganese-oxygen relationship was studied long ago by Körber and Oelsen<sup>4</sup> and more recently by Hilty and Crafts.<sup>5</sup> The carbon-oxygen reaction was investigated by Vacher and Hamilton<sup>6</sup> and by Marshall and Chipman.<sup>7</sup> A number of deoxidizing reactions have been studied empirically<sup>8-10</sup> with the object of determining the appropriate "deoxidation constants."

The work of Chen and Chipman<sup>11</sup> afforded a clear-cut view of the effect of the alloy element, chromium, on the thermodynamic activity of oxygen in liquid ternary solutions. These investigators determined the oxygen content of experimental melts which had been brought into equilibrium with a controlled atmosphere of hydrogen and water vapor and were able to show that the presence of chromium decreases the activity coefficient of oxygen. They determined also the conditions under which the two deoxidation products,  $Cr_2O_3$  and  $FeCr_2O_4$ , were formed and showed that the activity of residual oxygen is considerably less than its percentage.

It was the object of this investigation to apply a similar method to the study of molten alloys of iron, vanadium, and oxygen. Vanadium was once considered a moderately potent deoxidizer, but this is now known to be erroneous, in the light of its behavior in steelmaking practice. Its reaction with oxygen retains a certain amount of practical interest in that a high percentage of one element places a limit on the amount of the other that can be retained. As a deoxidizer it will be shown that vanadium lies between chromium and silicon.

## Experimental Method

The apparatus was that used by the authors<sup>3</sup> in their study of the equilibrium in the reaction:



Crucibles of Norton alundum or of pure alumina

were used. The latter were made in this laboratory and were of high strength and low porosity. Under conditions of use they imparted no significant amount of aluminum (less than 0.01 pct) to the bath. Temperature measurements were made with the optical equipment and calibration chart of Dastur and Gokcen.<sup>12</sup>

The charge was made up of calculated amounts of ferrovanadium (20 pct V) and clean electrolytic iron totaling approximately 70 g. The first few heats were made in alumina crucibles with an insufficient amount of vanadium so that no oxide of vanadium would be precipitated under the particular gas composition. All the heats were made at 1600°C under a high preheat and with four parts of argon to one part of hydrogen in the gas mixture to prevent thermal diffusion. The rate of gas flow was maintained constant at 250 to 300 ml per min of hydrogen. The time for each heat was three quarters of an hour after the melt had melted and attained the required temperature (1600°C).

The water-vapor content of the entrant gas mixture was gradually raised in succeeding heats, keeping the vanadium content of the melt constant. This was controlled by manipulation of saturator temperature. A point was reached when for a given  $H_2O:H_2$  ratio some of the dissolved vanadium was oxidized and appeared as a thin, bright oxide film on top of the melt. By raising the temperature of the melt it was possible to dissolve the oxide film which reappeared as soon as it was cooled down to 1600°C. The temperature readings taken on the oxide film were consistently higher by 80° to 85°C as observed by the optical pyrometer. The heat was allowed to come to equilibrium under a partial covering of this oxide film.

At the end of the run the power and preheater were shut off and the crucible containing the melt was lowered down into the cooler region in the furnace. This method of quenching proved quite

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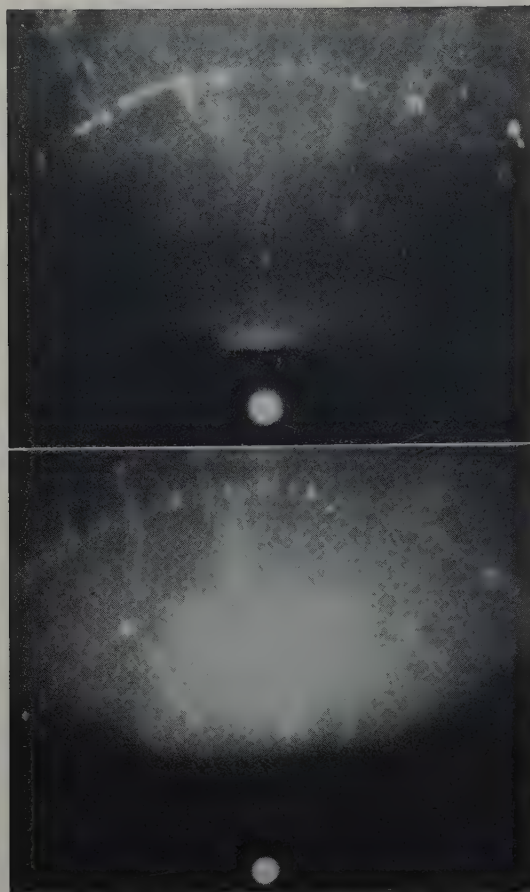


Fig. 1—X-ray diffraction photographs of oxide crusts.

a (above)—Heat No. 143 containing 0.90 pct V.  
b (below)—Heat No. 118 containing 0.10 pct V.

rium runs for saturated vanadium-iron melts, are marked with an asterisk in Table I.

### Identification of Oxide Phases

The oxide films formed on the surfaces of five typical ingots were examined by X-ray methods. The amount of film material was insufficient for use as a powder sample. Films were too thin to register a pattern by the back-reflection method. The forward-reflection Hull method was therefore employed using a pinhole camera. The X-ray beam from a chromium target was made to graze the specimen at a very acute angle so as to enable it to traverse as great a thickness of the oxide layer as possible.

The results for two ingots of high- and low-vanadium content are shown in Fig. 1 where the differences in pattern are clearly evident. Measurements of the observed patterns recorded in Table II agreed as well as could be expected for this method with the known patterns of  $V_2O_5$  and  $FeV_2O_4$ . The former was found on ingots containing more than 0.35 pct V. The latter, which is the spinel identified by Mathewson, Spire, and Samans,<sup>18</sup> was found on two ingots of 0.10 pct V.

Identification of the very small nonmetallic inclusions found in the ingots by microscopic examination was considerably less certain than the X-ray identification of the oxide films. Inclusions in low-vanadium ingots were of duplex structure containing wüstite and a dark phase, presumably the spinel. At higher vanadium levels wüstite disappeared and one or sometimes two dark phases were visible. In view of the inconclusive nature of this evidence, the identification rests solely upon the X-ray evidence.

effective, the solidification time never exceeding 10 sec.

### Results

Altogether 30 heats were made, of which 12 were unsaturated vanadium-iron alloy melts and 3 were discarded due to failure of some part of the apparatus or the breaking of a crucible. The equilib-

### Activity of Oxygen

It has been shown<sup>8</sup> that the value of  $K_1$  (eq 1) for pure iron-oxygen alloys at 1600°C is 3.95. In this case the activity of oxygen,  $a_o$ , is equal to its percentage by weight in the melt.<sup>1</sup> In the presence of vanadium the activity is found to be somewhat diminished; it becomes necessary, therefore, to in-

Table I. Fe-V-O Equilibrium Data at 1600°C

| Heat No. | Crucible Used                       | V Charged, Pct | $\frac{p_{H_2O}}{p_{H_2} \text{ corr.}}$ | V Analysis, Pct | Oxygen Analysis, Pct |        | Condition of Ingot |
|----------|-------------------------------------|----------------|------------------------------------------|-----------------|----------------------|--------|--------------------|
|          |                                     |                | Data                                     |                 | Chosen Value         |        |                    |
| 69       | Alundum                             | 0.44           | 0.0354                                   | 0.41            | 0.0132, 0.0132       | 0.0132 | Fair               |
| 70       | Alundum                             | 0.44           | 0.0442                                   | 0.41            | 0.0151, 0.0162       | 0.0156 | Sound              |
| 71       | Alundum                             | 0.44           | 0.0584                                   | 0.38            | 0.0196, 0.0190       | 0.0193 | Fair               |
| 72       | Alundum                             | 0.44           | 0.0790                                   | 0.38            | 0.0274, 0.0279       | 0.0276 | Sound              |
| 73*      | Alundum                             | 0.44           | 0.1050                                   | 0.31            | 0.0289, 0.298        | 0.0293 | Porous             |
| 74       | Alundum                             | 0.19           | 0.0363                                   | 0.134           | 0.0109, 0.0113       | 0.0111 | Sound              |
| 75       | Alundum                             | 0.19           | 0.0643                                   | 0.130           | 0.0186, 0.0186       | 0.0186 | Porous             |
| 76       | Alundum                             | 0.19           | 0.0839                                   | 0.125           | 0.0221, 0.0225       | 0.0223 | Sound              |
| 77       | Alundum                             | 0.19           | 0.1049                                   | 0.128           | 0.0302, 0.0304       | 0.0303 | Sound              |
| 78       | Alundum                             | 0.19           | 0.1390                                   | 0.120           | 0.0373, 0.0381       | 0.0377 | Sound              |
| 95       | Alundum                             | 0.93           | 0.0294                                   | 0.83            | 0.0133               | 0.0133 | Fair               |
| 96       | Alundum                             | 0.93           | 0.0419                                   | 0.83            | 0.0178, 0.0194       | 0.0186 | Sound              |
| 98*      | Alundum                             | 0.93           | 0.0530                                   | 0.80            | 0.0227, 0.0231       | 0.0229 | Sound              |
| 107*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.93           | 0.0606                                   | 0.75            | 0.0221, 0.0234       | 0.0227 | Sound              |
| 108*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.19           | 0.226                                    | 0.090           | 0.0640, 0.0626       | 0.0633 | Sound              |
| 109*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.19           | 0.2790                                   | 0.053           | 0.0733, 0.0750       | 0.0742 | Sound              |
| 111*     | Alundum                             | 1.58           | 0.0352                                   | 1.16            | 0.0214, 0.0228       | 0.0221 | Porous             |
| 112*     | Alundum                             | 1.58           | 0.0389                                   | 1.31            | 0.0231, 0.0182       | 0.0207 | Porous             |
| 113*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.13           | 0.3210                                   | 0.032           | 0.0835, 0.0874       | 0.0854 | Sound              |
| 114*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.32           | 0.2086                                   | 0.098           | 0.0514, 0.0496       | 0.0505 | Sound              |
| 115*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.66           | 0.0985                                   | 0.365           | 0.0328, 0.0309       | 0.0319 | Fair               |
| 116*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.79           | 0.0689                                   | 0.536           | 0.0249, 0.0247       | 0.0248 | Fair               |
| 117*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.53           | 0.1048                                   | 0.358           | 0.0324, 0.0329       | 0.0326 | Sound              |
| 118*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.26           | 0.2048                                   | 0.099           | 0.0529, 0.0512       | 0.0521 | Sound              |
| 119*     | Pure Al <sub>2</sub> O <sub>3</sub> | 1.58           | 0.0312                                   | 1.25            | 0.0181, 0.0178       | 0.0180 | Sound              |
| 120*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.47           | 0.1132                                   | 0.259           | 0.0325, 0.0349       | 0.0337 | Sound              |
| 121*     | Pure Al <sub>2</sub> O <sub>3</sub> | 0.37           | 0.1670                                   | 0.150           | 0.0413, 0.0415       | 0.0414 | Sound              |

\* Iron-vanadium alloys saturated with oxygen.



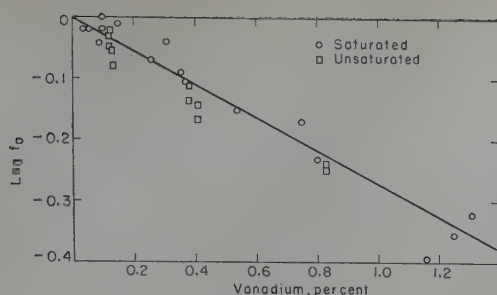
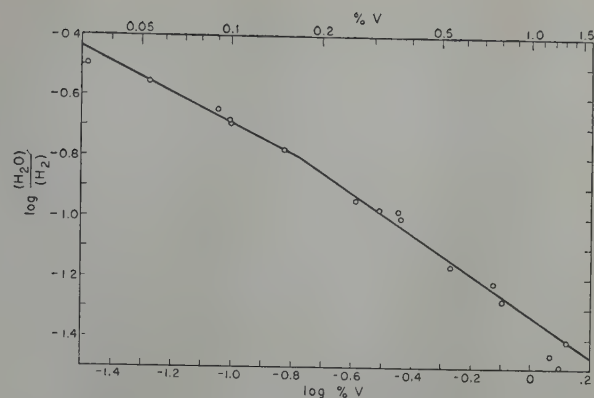


Fig. 2 (above)—Effect of vanadium on the activity coefficient of oxygen,  $f_o$ .

Fig. 3 (right)—Equilibrium in the reaction of water vapor with vanadium in liquid iron at 1600°C. Above the break, the oxide is  $V_2O_3$ ; below the break,  $FeO \cdot V_2O_3$ .



introduce an activity coefficient,  $f_o$ , defined by the equation:

$$f_o = a_o / \% O$$

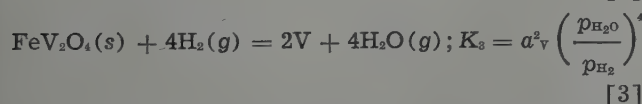
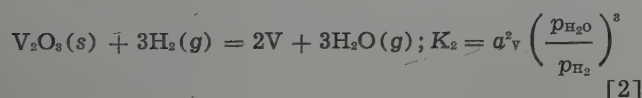
The equilibrium constant of eq 1 becomes:

$$K_1 = \frac{p_{H_2O}}{p_{H_2} \cdot f_o \cdot \% O} \quad [1a]$$

Using the value  $K_1 = 3.95$ , values of  $f_o$  are readily obtained for each heat of Table I. These are shown in Fig. 2 where the logarithm of  $f_o$  is plotted against the percentage of vanadium. The straight line represents adequately both saturated and unsaturated heats. The effect of vanadium on the activity coefficient of oxygen is considerably larger than that reported for chromium.<sup>11</sup>

### Reaction of Vanadium with Water Vapor

If we assume that either of two solid phases occurred in the films found on the saturated heats, and that these have compositions corresponding to the structures indicated by X-ray diffraction, the equations for the two equilibria may be written:



It may be assumed that the solution is dilute enough to conform to Henry's law and hence that the activity of vanadium may, by definition, be placed equal to its percentage by weight.

The data on all saturated heats are plotted in Fig. 3. A logarithmic scale is used and two lines are drawn having slopes of 3:2 and 4:2 corresponding to the requirements of eqs 2 and 3, respectively. These two lines fit the data fairly well except for

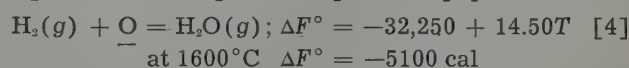
some deviation at the highest vanadium level. This deviation may be attributed to departure from Henry's law or possibly to the appearance of a third (lower) oxide phase, but there is no evidence of either and it may be regarded as the result of experimental inaccuracy. The two lines intersect at 0.17 pct V at which composition the two oxide phases coexist in equilibrium with the melt at 1600°C.

The equilibrium constants and free energies of reactions 2 and 3 corresponding to the two lines of Fig. 3 are, at 1600°C:

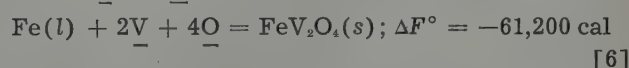
$$K_2 = 1.1 \times 10^{-4}; \Delta F^\circ_2 = +34,000 \text{ cal} \quad [2a]$$

$$K_3 = 1.7 \times 10^{-5}; \Delta F^\circ_3 = +40,800 \text{ cal} \quad [3a]$$

The free-energy change in the deoxidation of steel by vanadium is obtained by combining these two equations with eq 1 of the previous paper which is:



This yields the following values for the two free-energy changes at 1600°C:



The experimental data are insufficient to express the free energy as a function of temperature. Approximate equations covering this relationship will be derived in a later section.

### Comparison with Low-Temperature Data

The free energy of  $V_2O_3$  is obtained from its heat of formation at 25°C which, according to Siemonsen and Ulich,<sup>14</sup> is -296 kcal, and entropy values given by Kelley.<sup>15</sup> The heat capacities of V and  $V_2O_3$  in the range 25° to 1600°C are taken respectively from Jaeger and Veenstra<sup>16</sup> and Cook.<sup>17</sup> The result, for

Table II. X-Ray Diffraction Patterns of Oxide Films

| Vanadium Content, Pct |           |      |           |      |           |      |           |      |           | Theoretical Pattern |       |           |
|-----------------------|-----------|------|-----------|------|-----------|------|-----------|------|-----------|---------------------|-------|-----------|
| 0.90                  |           | 0.54 |           | 0.36 |           | 0.10 |           | 0.10 |           | Due to              | d     | Intensity |
| d                     | Intensity | d    | Intensity | d    | Intensity | d    | Intensity | d    | Intensity |                     |       |           |
| 3.65                  | M         | 3.68 | S         | 3.67 | S         |      |           |      |           | $V_2O_3^*$          | 3.65  | M         |
| 2.95                  | VW        |      |           | 2.98 | VW        | 2.99 | S         | 2.99 | M         | $FeV_2O_4^\dagger$  | 2.994 | M         |
| 2.70                  | VS        | 2.72 | VS        | 2.72 | VS        |      |           |      |           | $V_2O_3$            | 2.70  | S         |
|                       |           |      |           |      |           | 2.53 | S         | 2.54 | S         | $FeV_2O_4$          | 2.552 | VS        |
| 2.48                  | W         | 2.48 | VW        |      |           |      |           |      |           | $V_2O_3$            | 2.47  | M         |
| 2.21                  | VW        |      |           |      |           |      |           |      |           | $V_2O_3$            | 2.18  | W         |

Notes: S = strong; M = medium; W = weak; V = very. \*ASTM data card No. 3655. †Ref. 13.



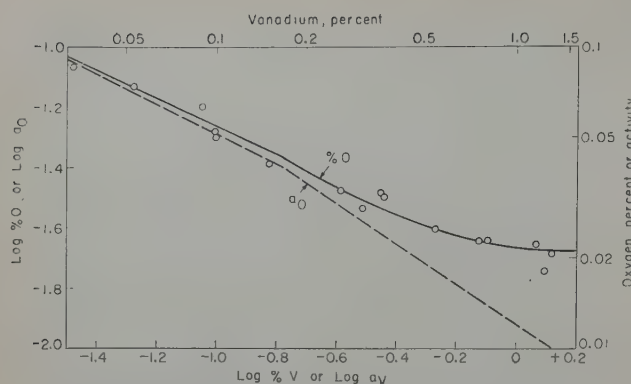
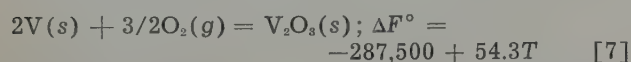
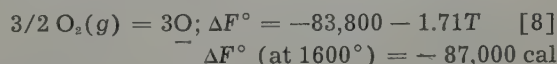


Fig. 4—Deoxidation diagram for vanadium in steel at 1600°C. Lower line shows oxygen activity; upper line, oxygen percentage in equilibrium with solid  $V_2O_5$  or  $FeV_2O_4$ .

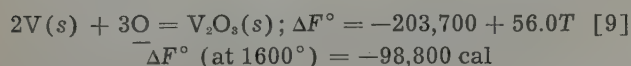
a temperature range of 1400° to 1700°C, may be expressed in the simple form:



For comparison with our experimentally determined free energy we must subtract from this the free energy of solution of 3/2 mol of oxygen in liquid iron. From our previous paper<sup>3</sup> this is:



The result is:



The next step in the computation requires the free energy of solution of solid vanadium in the dilute solution corresponding to the experimental range. This information is lacking altogether. Instead of assuming that the solution is ideal, the comparison of calculated and observed free energies will be completed by computing the deviation of the solution from Raoult's law. For this purpose eq 5 is subtracted from 9 to obtain:



Now if vanadium formed an ideal solution in iron, this free-energy change could be computed by well-known methods which are adequately discussed in "Basic Open Hearth Steelmaking."<sup>18</sup> The heat of fusion of vanadium has not been measured but, since temperatures not far below its melting point are the concern here, the error introduced by this uncertainty is entirely negligible. Taking the entropy of fusion as 2.1 cal per degree mol, the free-energy change for eq 10 is computed as -16,700 cal. The discrepancy of 8000 cal is greater than the probable errors of the subsidiary data, although earlier values for the heat of formation of  $V_2O_5$  differed by 34,000 cal from that used here. It will be assumed that the 8000 cal represents the actual deviation from Raoult's law of the ideal solution.

The activity coefficient of vanadium in the dilute solution, defined here as the ratio of its activity to its mol fraction, is computed by equating the deviation -8000 cal to  $RT \ln \gamma^\circ$  from which:

$$\gamma^\circ = 0.12 \quad [11]$$

To apply this to temperatures other than 1600°, the deviation from Raoult's law will be attributed to a heat of solution of vanadium in iron, i.e., it will be assumed that the solution is "regular" and that the

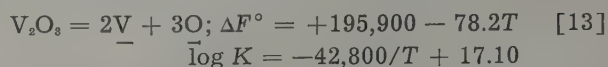
deviation is not in the entropy. The resultant equation is:

$$V(s) = \underline{V}; \Delta F^\circ = -3900 - 11.1T \quad [12]$$

It should be stressed that eqs 10, 11, and 12 are approximations which depend upon thermochemical data of unproved accuracy. An error of 5 kcal in the heat of formation of  $V_2O_5$  would correspond to a factor of 2 in the value of  $\gamma^\circ$ . It seems safe to conclude that the vanadium-iron solution exhibits negative deviation from Raoult's law and that  $\gamma^\circ$  is probably less than 0.25.

### Effect of Temperature on Equilibria

Since all the experimental data were obtained at 1600°C, the effect of temperature can be learned only through calculations. The foregoing equations provide the basis for a very reasonable approximation. Combination of eqs 9 and 12 gives:



Available data are insufficient for a similar calculation of the equilibrium involving the spinel.

### Deoxidation with Vanadium

Although vanadium is not used as a deoxidizer in practice, its behavior in the deoxidation reaction illustrates a principle which is applicable to all such reactions. It has been shown that the activity coefficient of oxygen is strongly decreased by the presence of vanadium. The deoxidation constant corresponding to equilibrium in eq 13 must be expressed in terms of the activities of vanadium and oxygen, thus:

$$K = a_V^2 \cdot a_O^3 = [f_V \cdot \% V]^2 [f_O \cdot \% O]^3 \quad [13a]$$

Values of  $K$  at 1500°, 1600° and 1700°C are  $1.0 \times 10^{-7}$ ,  $1.8 \times 10^{-6}$  and  $2.6 \times 10^{-5}$ .

In Fig. 4 the lower line represents the activity of oxygen corresponding to any concentration of vanadium for metal in equilibrium with  $V_2O_5$  at 1600°C. Since the oxygen concentration is small its effect on the activity of vanadium is considered negligible.

The upper line of Fig. 4 shows the experimentally determined oxygen content of the same metal. The two portions of each curve intersecting at 0.17 pct V correspond to equilibrium with  $V_2O_5$  above and  $FeV_2O_4$  below the intersection.

This deoxidation diagram proves to be somewhat more complex than its earlier prototypes. At the same time it contains a greater amount of information. It displays the two-fold effect of a deoxidizing element in reducing not only the solubility of oxygen in the melt but also the activity of that oxygen which remains. The question of whether, in a given case, the upper or the lower line is used must depend upon the information desired, that is, how much oxygen is in solution in the metal or how that oxygen behaves.

### Summary

An experimental study has been made in which molten iron-vanadium alloys containing 0.03 to 1.3 pct V were brought into equilibrium with controlled atmospheres of water vapor and hydrogen at 1600°C. When the gas mixture is sufficiently oxidizing, an oxide film forms on the metal surface. This was identified as  $V_2O_5$  on melts containing 0.36 pct or more, and as the spinel  $FeV_2O_4$  on melts containing 0.10 pct V.

From the oxygen content of the melts and the



known value of  $K_1 = p_{H_2O}/(p_{H_2} \cdot a_O)$  in pure iron, the activity of oxygen in the alloy was obtained. Vanadium decreases the activity coefficient of oxygen, the logarithm of the latter being proportional to the concentration of vanadium.

A deoxidation diagram is presented in which two lines show respectively the percentage and the activity of oxygen in the alloy. Each line shows a change in slope at approximately 0.17 pct V. Above this concentration the solid phase is  $V_2O_5$ , and below it is  $FeV_2O_4$ .

#### Acknowledgment

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#### Technical Note

### "Oriented Growth" in Primary Recrystallization

by Joseph J. Becker

RECENTLY the "oriented growth" hypothesis of recrystallization textures has been receiving considerable attention. According to this view, "when ever a new generation of grains is growing in a highly oriented matrix . . . one may assume . . . that from among available nuclei of a great variety of orientations those with suitable orientation relationship with respect to the matrix have by far the highest rate of growth (oriented growth) and will, therefore, predominate."<sup>1</sup> This statement includes primary recrystallization of single crystals and of polycrystalline materials showing strong deformation textures as particular cases. While the phenomenon of oriented growth undoubtedly does operate, and may be of importance in coarsening or secondary recrystallization, the writer feels that its extension to primary recrystallization is a different matter. Several aspects of this phenomenon may be pointed out which are difficult to rationalize on the basis of oriented growth.

In recrystallizing deformed single crystals of alpha brass, Maddin, Mathewson, and Hibbard<sup>2</sup> found that the twin composition planes of the recrystallized grains were parallel to the three operative slip planes they observed, and not to the fourth octahedral plane. The writer's current work seems to indicate further that when only one or two slip systems can be seen to operate, the recrystallized grains are aligned only with those slip planes actually observed. This behavior could hardly be accounted for by oriented growth, because on the latter basis the recrystallized texture of a deformed single crystal should certainly have the same symmetry as the crystal itself. Growth rates could not be expected to distinguish between crystallogra-

phically equivalent directions, unless the presence of a visible slip system vastly increases the growth rate in the appropriate direction. This seems unlikely.

These relationships were observed by the writer only when considerable care had been exercised before annealing to etch away the effects of cutting out the centers of tensile specimens with a jeweler's saw and to etch off the ends of compression specimens. When these precautions were not taken, nucleation inevitably appeared to occur at the saw cuts or at the ends, and the resulting orientations never showed a [111] rotation but appeared quite random. The provision of many nuclei of many orientations did not enhance the correlation, but destroyed it.

Recrystallization textures are sometimes strongly dependent on annealing temperature, which would imply that the anisotropy of growth rates is a suddenly varying function of temperature. This might be regarded as unlikely.

Recrystallization textures can be strongly dependent on the degree of deformation. If textures are to be explained by selective growth from among nuclei of all orientations, it is difficult to see how the recrystallization process could have any dependence whatever on the manner or degree of deformation.

It is felt that the above points should be considered before the oriented growth hypothesis is applied to primary recrystallization, with the necessary complete divorce of the mechanism of recrystallization from the details of the deformation process.

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TN 52E. Manuscript received Oct. 2, 1950.



# Sintering Practice At Josephtown Smelter

by H. K. Najarian, Karl F. Peterson,  
and Robert E. Lund

**P**RIMARY products of the Josephtown smelter are zinc metal of various grades, lead-free zinc oxide pigments, cadmium metal, and sulphuric acid. Zinc concentrates of domestic and foreign origin are blended and desulphurized at the roaster plant. The equipment includes five, 12-hearth Herreshoff roasters and two modified Trail-type suspension roasters. The sulphur dioxide containing gases from the roasting operation are diverted to a four-unit contact acid plant for the manufacture of sulphuric acid. The roasted calcines are agglomerated by sintering on Dwight-Lloyd-type sintering machines; the sinter is crushed and sized within required limits; and the sized sinter is smelted in vertical shaft-type electrothermic furnaces. Of the 13 electrothermic furnaces of various sizes now in operation, four are designed to produce American process zinc oxide of various specifications; and the remaining nine furnaces are equipped with vacuum-type condensers and produce zinc metal. Papers describing the general smelting practice at Josephtown have been published by AIME.

Since both High Grade zinc metal and lead-free zinc oxide pigments are produced direct from the electrothermic furnaces without need for subsequent refining, the elimination of impurities such as lead and cadmium has to be accomplished during roasting and sintering operations.

To effect the producing of both High Grade and Prime Western zinc products, the roasting and sintering operations are on two separate circuits. A High Grade circuit produces finished sized sinter low in lead, cadmium, etc., for the High Grade furnaces; and the Prime Western circuit produces finished sinter destined for the furnaces producing Prime Western metal.

Sintering at the Josephtown smelter differs in many important respects from the sintering practice in smelters operating horizontal retort zinc furnaces. Requirements of the electrothermic smelting furnaces define the physical characteristics of the sinter, while the chemical composition of the sinter is controlled according to the grade of metal and oxide to be made as final products. Three principal objectives in the sintering process at Josephtown smelter are:

1. To transform the zinc calcine from the roasting operations into a hard, yet porous agglomerate that will not crumble in the smelting furnace.

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2. Crushing and sizing of the sinter to obtain a proper screen analysis which is normally  $-\frac{3}{4}$  in. down to  $+\frac{1}{4}$  in. particle size.

3. To eliminate, particularly in the High Grade circuit, as much of the impurities such as sulphur, lead, and cadmium as possible.

The sintering plant as originally built in 1930 was equipped with three standard 42 in. x 44 ft Dwight-Lloyd sintering machines. Each machine was equipped with a 15x60 in. sintering corporation fan driven by 150 hp, 900 rpm synchronous motor through a magnetic clutch and capable of delivering 30,000 cfm of air at 15 in. of water and 150°F. Each sintering machine was driven by 7½ hp dc motor with controllers for varying the speed of the machine from 8 to 32 in. per min. The pallets were cast iron and the grates of the herringbone type. The charge was mixed in a 4 ft diam x 8 ft Stehli pugmill and transported by belt conveyor, elevator and tripper conveyor to a small bin over each machine.

Shortly after the start of operations the following changes were found necessary:

1. The herringbone grates which plugged very quickly and were difficult to keep clean were replaced by straight, narrow cast-iron grate bars running at right angles to the travel of the pallets. These grate bars are held in place by a center bar extending across the pallet on the 24 in. dimension and by removable retaining plates which form the sides of the pallets.

2. Mechanical grate knockers were developed in conjunction with new grate bars for continuously and automatically cleaning the grates.

3. As the cast-iron pallets cracked, they were replaced with cast-steel pallets.

In 1938, the capacity of the sinter plant was increased with the installation of two 42 in. x 22 ft machines which were brought from the company's Herculeaneum lead smelter. With a circulating load of some 250 to 300 pct, production of finished sinter on the 42 in. x 44 ft machines at this time amounted to about three tons of sized sinter per machine hour.

In 1945, one of the 42 in. x 22 ft machines was replaced by a 60 in. x 44 ft machine of our own design.

In 1948, as part of the plant-wide expansion program, the sinter plant not only was expanded but also divided into two separate plants; namely, Prime Western and High Grade circuits. The sinter destined for furnaces producing Prime Western zinc metal is made in a new plant comprising two 60 in. x 44 ft Dwight-Lloyd-type sintering machines, each having a 45,000 cfm Sturtevant fan at 18 in. water static pressure and served by an 8 ft diam x 12 ft long rotary charge pelletizer and auxiliary crushing and sizing equipment. The sinter destined for furnaces producing High Grade zinc metal and zinc oxide pigments is produced in the old sinter plant which was expanded to accommodate four of the 60 in. x 44 ft sintering machines, replacing the old sintering units. In the High Grade sinter circuit, two units of the 60 in. x 44 ft machines are used as preliminary soft sinter machines; and the remaining two units of the 60 in. x 44 ft machines are used to make finished hard sinter.

## Purification Theory

Partial elimination of lead and cadmium in the sintering of zinc ores is common knowledge. However, by some manipulation and by taking advantage of the double circuit, it is possible to make zinc sinter which is nearly free of contaminators. Lead



and cadmium, both being more easily reduced with carbon than zinc and being quite volatile in the sulphide form, are driven ahead of the intensely hot burning zone in the sinter cake. On the soft sinter machines, the charge is quite refractory; therefore little slagging takes place during the burning of the charge. The top part of the bed is more nearly free of impurities than the bottom due to condensation of lead and cadmium compounds at the grate area.

It is important to have an open fast-burning charge and a high fusion point charge in order to get good elimination. Equally as important is a charge with the proper amount of fuel and moisture. Our experience has shown 4 to 4.6 pct coke is necessary with a calcine sulphur of from 1 to 3 pct.

To produce a sinter of requisite hardness, it is necessary to add to the charge enough silica sand to obtain 8 to 9 pct  $\text{SiO}_2$  in the finished sized sinter. However, addition of this silica to the sinter mix inhibits the elimination of lead and cadmium during sintering. Therefore the low-lead calcines brought in to this High Grade sinter circuit from the roaster plant are given a preliminary soft sintering without the addition of silica sand. This results in the elimination of 80 pct of the lead and some 90 pct of the cadmium and sulphur.

The product of the soft sintering step is resintered with the addition of silica sand and some intermediate products to produce the finished, hard sized sinter required for the High Grade furnaces.

### Prime Western Sintering Circuit

The feed for the Prime Western sintering circuit comprises very fine suspension roaster calcines, —3/16 in. residues from the Prime Western furnaces, and dust collected in the Dracco collector from sinter, coke, residue, and furnace plants.

A typical charge going to the Prime Western machines is, in pounds per minute: calcine, 250; Dracco dust, 200; residue fines, 100; coke (—8 mesh), 50; sand (about 30 mesh), 8; and circulating return sinter, 1000.

All of these charge components are stored in steel storage feeder bins of adequate capacity. From the storage bins, calcines and Dracco dust are fed by screw feeders and the remaining components are fed by belt-type feeders on to a collecting screw conveyor which delivers it to an elevator discharging directly into a rotating pelletizer. The mixed charge contains about 4.4 pct coke fuel, part of which comes in through the Dracco dust and the residue fines. The residue fines in the charge are that portion of the reclaimed high-zinc furnace residues which passes through a 3/16 in. screen opening. The charge material is mixed quite thoroughly while the material is being conveyed through the screw conveyors and the elevator to the pelletizer. This unit is 8 ft in diam and 12 in. long. It rolls on two large steel tires and is driven by a 15 hp motor directly connected to a speed reducer, which is in turn connected to an 18 T-8 in. F spur gear driving the ring gear that encircles the drum. The discharge end is completely enclosed and vented to a sinter machine wind box.

In the pelletizer, the charge is moistened with water or dilute zinc sulphate solution by means of a pipe spray so designed that the solution is sprayed on the material during its entire passage through the pelletizer. The wetting solution is a byproduct of the leaching operations plus run-off water from Cottrell conditioning chambers. It has been found that a small amount of zinc sulphate in the spray

water in the pelletizer promotes adherence of fine particles to the larger granular particles, resulting in more or less rounded pellets of various sizes. This, experience shows, makes an ideal feed for sintering.

The mix in the pelletizer tends to stick and build up on the inside of the pelletizing drum. A ribbon screw, rotating independently of the pelletizer and contacting the inside periphery of the pelletizer drum near the horizontal center line, continuously cleans the inside of the drum. The drum rotates at about 17 rpm and the cleaner screw at about 80 rpm, both in the same direction.

The pelletized feed is discharged onto a rotating table where two plows split the feed and transfer it to belt conveyors which in turn carry it to the feed end of the sintering machines. The charge drops onto the grates through a rubber-covered swing spout which distributes the charge across the grates in an even fashion, allowing the coarser particles to roll onto the bare surface of the grates. The sintering machine speeds are maintained so that the charge is kept as low as possible behind the spreader plate so as to maintain a fluffy charge. The density at this point is about 130 lb per cu ft.

The charge is ignited by a gas-fired muffle using byproduct CO from the zinc condensers as fuel. Sintering machine speeds vary between 12 and 16 in. per min depending on rapidity of burning. The draft on the wind boxes will average 13 in. of water, varying from as low as 9 in. to as high as 18 in. depending on the condition of the charge. A dense, poorly pelletized charge will be slow burning and have a high wind-box draft. The operator changes the charge as conditions dictate. If for some reason the charge becomes tight and will not burn as rapidly as mix is being fed onto the machines, the condition soon is aggravated by unburned mix appearing in the return sinter. To remedy this, the operator cuts the volume of new charge in the mix; that is, calcine, residue fines, and Dracco dust so that the machine can be run more slowly and allow more time for burning. Proper moisture in the mix is very important to good charge preparation. Our experience has been that 9½ to 11 pct moisture, depending somewhat on the fineness of the material and the ratio of fines to coarse, gives good results. The charge is approximately 97 pct —¼ in. and 35 pct —200 mesh. Charge thickness on grates is carried at approximately 11 in.

A 35 to 40 pct —200 mesh material in the mix has been found to be essential for obtaining a good pelletized charge. Our experience has shown that a pelletized charge comprising rounded granules permits freer passage of gases through the sinter bed and is far superior to a charge of angular particles of various sizes with fines filling the interstices.

The sinter cake as discharged from the machines usually shows a small red hot zone in the lower part of the bed. The cake is broken into some one half dozen pieces as it drops 8 ft onto a 36 in. wide pan conveyor. The pan conveyor carries the sinter to a 24x42 in. toothed slugger rolls which crushes the chunks to —3 in. Sizing is accomplished by first screening the product of the rolls over a rotating trommel having ¾ in. openings. The oversize from the trommel is crushed again in a smooth-faced 36 in. diam x 16 in. face rolls set ⅝ to ¾ in. apart. Roll product is returned to the trommel and a large circulating load is maintained in order that a minimum of fines is produced. The —¼ in. return sinter is separated by screening through a trommel having



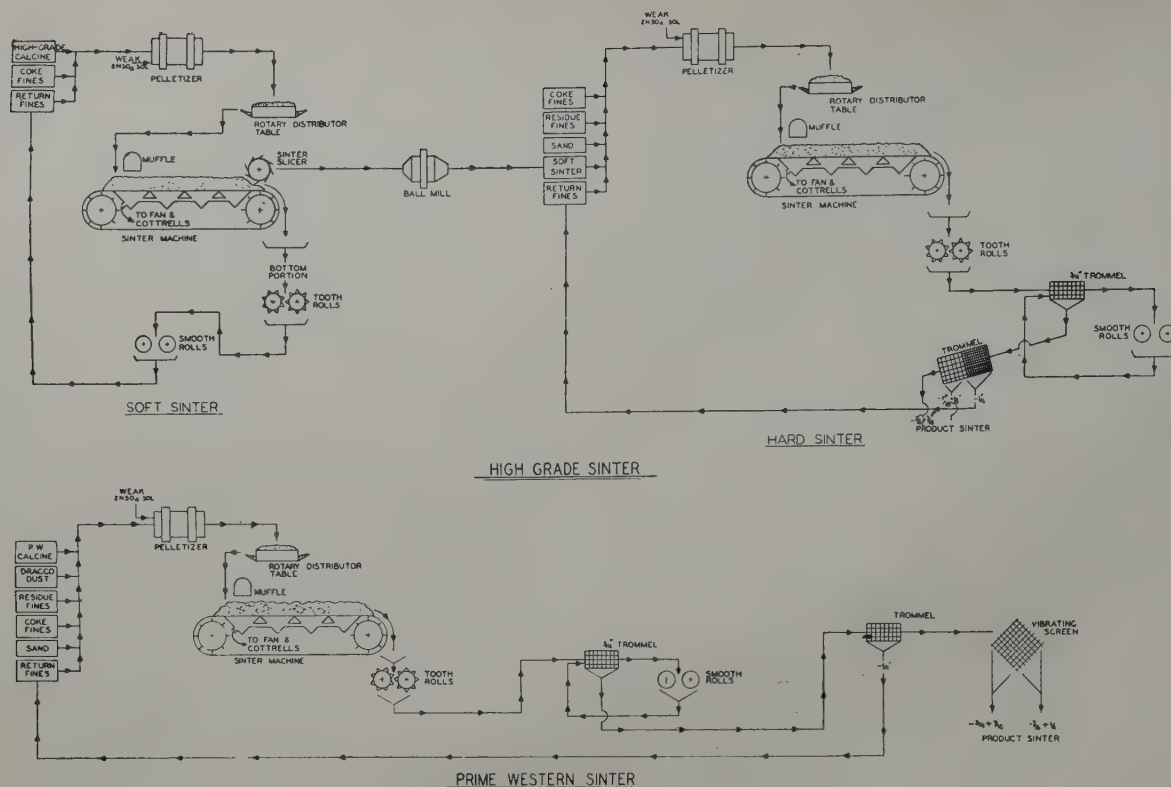


Fig. 1—Sinter circuits of Zinc Smelter Division.

$\frac{1}{4} \times \frac{3}{4}$  in. slotted openings. The oversize of this screen is again screened over a  $\frac{7}{16}$  in. screen to make two finished products which are blended to give a uniform sinter size.

The sizing of the sinter feed to the furnaces is very important for proper charge distribution in the furnaces. A typical screen analysis of this sized sinter is as follows:  $-\frac{3}{4} + \frac{1}{2}$  particle size, 35 pct;  $-\frac{1}{2} + \frac{3}{8}$ , 20;  $-\frac{3}{8} + \frac{1}{4}$ , 32; and  $-\frac{1}{4}$ , 8. A typical chemical composition is: Zn, 55.0 pct; Pb, 0.65; S, 0.2; Cd, 0.01; Fe, 10.0;  $\text{SiO}_2$ , 8.7; and MgO and CaO, 1.2.

### High Grade Sintering Circuit

Sintering in the High Grade circuit is in two separate steps. Low-lead calcine from the roasting plant is sintered first without the addition of silica sand to the charge. The resulting product is a soft, easily crushed sinter of high purity. The lead content is 0.005 pct or less, the cadmium content is 0.001 pct or less, and the sulphur content is 0.1 pct. The top half of the soft sinter cake containing the least amount of impurities is removed by means of a rotary slicer, mixed with silica sand, residues from furnaces using High Grade sinter, coke and return fines and sintered a second time to produce the hard, sized sinter which constitutes the feed to the High Grade metal and oxide furnaces.

Of four units of 60 in. x 44 ft Dwight-Lloyd sintering machines in the High Grade circuit, two are used for the soft sintering step and the other two for the hard sintering step.

### Soft and Hard Sintering

A typical charge mix for soft sintering is: low-lead calcines (about 0.05 pct Pb), 400 lb per min; return sinter (crushed), 1000 lb per min; and coke ( $-8$  mesh), 65 lb per min.

An 8 ft x 72 in. Allis Chalmers ball mill is being installed to grind the calcines to insure enough fines (35 to 40 pct  $-200$  mesh) for proper pelletization

of the mix. The return sinter is the bottom portion of the sinter cake crushed to  $-\frac{1}{2}$  in.

The portion of the cake left on the pallet after removing the top is discharged onto a 36-in. pan conveyor which carries it to the 24x42 in. slugger rolls. The product of the slugger rolls, all  $-1$  in., is transferred by means of a 24-in. pan conveyor to a 20 in. diam x 20 in. face smooth rolls set at  $\frac{5}{8}$ -in. opening. The crushed product is conveyed by an elevator and 24-in. pan conveyor to the soft sinter "return fines" bin to be recirculated over the soft sinter machines.

As in the Prime Western sintering circuit, the constituents of the hard sinter mix are fed from respective storage bins by constant volume feeders. This mix is transported to a 6x12 ft rotary drum pelletizer which discharges the pelletized mix onto a rotating table feeder and thence to two sinter machines.

### Sinter Slicers

The slicers on the discharge ends of the soft sinter machines are in the form of a double drum inside of which is a 16 in. screw flight. The outside drum contains cutters tangent to the drum and extending out to be approximately 4 in. from the circumference of the drum. Four of these knives are placed about the circumference of the drum  $90^\circ$  apart and extending the full length of 4 ft 6 in. The cutters are rotated at 20 rpm by means of a 15 hp motorized reducer. Power is transmitted by means of a chain and sprockets. As the drum rotates, it cuts off approximately  $\frac{1}{2}$  in. of charge as deep in the bed as is desired and drops the cuttings into a slot in the inner drum where the screw conveys it to the end and discharges into a chute on one side of the sinter machine. This is the product of these machines. That part which is not taken off by the slicer after burning is crushed to  $-\frac{1}{2}$  in. and recirculated.

The product of the sinter slicer which cuts the top  $\frac{1}{3}$  to  $\frac{1}{2}$  of the soft sinter cake is granular, largely



— $\frac{1}{4}$  in., and contains the least percentage of contaminants such as lead and cadmium. An 8 ft x 72 in. wind-swept Hardinge mill is being installed to grind this material so as to provide some 35 to 40 pct —200 mesh material, the product necessary for good pelletizing of the sinter mix. This ground product, high zinc residues from the High Grade furnaces, coke, silica sand, and return fines, constitute the charge for the High Grade sinter circuit.

A typical charge to High Grade hard sinter circuit sinter machines in pounds per minute is: ground soft sinter, 450; High Grade residue fines, 180; return sinter fines, 1000; silica sand, 10; and coke, 62.

Feeding the various mix constituents, conveying, pelletizing and sintering, crushing and screening are essentially a duplicate of the Prime Western sintering circuit. The product of this plant is a sized hard sinter and is used on all furnaces producing High Grade metal and oxide pigments.

Sizing is carried on in the same manner and with the same standards as were previously mentioned in the discussion of the Prime Western circuit.

Typical chemical analysis of the High Grade sinter is: Zn, 56 pct; Pb, 0.004; S, 0.1; Cd, 0.003; Fe, 10; SiO<sub>2</sub>, 8.7; and CaO and MgO, 1.2.

### Dust Collector

A very important part of the sintering plant is the Dracco dust collector. The unit is made up of 56 individual compartments each containing 80 tapered woolen bags. The bags measure 113 in. long, 6 in. in diam on the top end and 8 in. in diam on the bottom end. Filter rate is from 3.7 to 5.2 cu ft per min per sq ft of bag area. The pressure drop across the bags is from 4 to 5 in. of water. This baghouse takes care of the major part of the dust produced at material transfer points in the sintering, residue, and furnace plants. Suction is supplied by a 12 ft diam Buffalo fan directly connected to a two-speed motor. At low speed, the fan is capable of delivering 200,000 cfm at 8 in. water static pressure and uses a 400 hp, 514 rpm motor. At high speed, the fan rotates at 600 rpm, is driven by a 600 hp motor and will deliver 275,000 cfm at 9½ in. water static pressure. The fan is operated at high speed during the day shift while the furnace plant operations require additional dust removal capacity. Approximately 85,000 cfm is allocated to the sintering plant for dust removal. Approximately 80 tons of dusts are collected each 24 hr and returned to the Prime Western sinter circuit through this baghouse unit.

### Cottrells

An integral appendage to the sintering plant is the Cottrell installation for recovery of fume from the sintering machine gases. Sintering machine gases are discharged from the machine fans into large spray conditioning chambers for humidification prior to entering the Cottrells. Three separate Cottrell precipitators serve the sintering plant. Two precipitators, each rated at 100,000 cfm, receive gases from the hard sinter and soft sinter machines of the High Grade circuit. A precipitator of 150,000 cfm rating was installed to serve the Prime Western circuit with anticipation of expansion to include a third Dwight-Lloyd machine.

Cottrell precipitators were installed by Research Corp. and are of the rod-curtain type. Shell construction is of concrete with a 1-in. ceramic lining. Each precipitator comprises four sections, two in series and two in parallel. Each section in the 100,000

cfm precipitators consists of 21 ducts while the 150,000 cfm precipitator sections contain 27 ducts. Rated gas velocity is approximately 4 fps with a total treatment time of 5 sec. Gas flow is horizontal. High voltage supply for ionization of the gases in each Cottrell is furnished by three transformers of 75,000 v, 25 kva rating with associated mechanical rectifiers.

Proper conditioning of the gases entering the Cottrells is essential for efficient collection. In general terms, the absolute humidity of the gases is maintained as high and the dry bulb temperature as low as physical conditions of the collected dust and corrosion limitations permit. Gases entering the conditioning chambers are cooled to a dry bulb temperature of 130° to 135°F before entering the Cottrells. Absolute humidity is 9 to 11 pct by volume with corresponding relative humidity in the range of 70 pct. Operators maintain optimum precipitator voltage and corona current by transformer tap and rheostat adjustments. All three rectifiers of each Cottrell are operated continuously, one is connected to both inlet sections, and one each to outlet sections. Care is given to cleaning Cottrell electrode members and to proper gas distribution. Precipitators are inspected daily to insure effective rapper operation and clean gas distributing plates.

Dust collected by the Cottrells averages approximately 2 pct of the calcine and soft sinter feed to the sintering machines. This dust is collected in large hoppers under the precipitating chamber. There are two hoppers to each half of the precipitator, each equipped with a 9-in. screw conveyor which feeds into a long, 12-in. collect conveyor. The dust is conveyed to a tank where it is slurried with acid plant scrubber effluent and pumped to the leaching plant for further treatment. Recovery of metallic compounds from the flue gases averages 90 to 95 pct with corresponding exit dust loadings from the Cottrells of about 0.01 grains per cu ft.

A typical analysis of the collected fume from the Prime Western machines is: Zn, 30 pct; Cd, 7; Pb, 9; total S, 10; sulphide S, 5; and Cl, 1.

The conditioning chambers associated with each Cottrell are of acid-proof brick construction and built in two separate units. Each unit averages 27 ft high, is 50 ft deep, and 15 ft wide on the 150,000 cfm Cottrell, 12 ft wide on the 100,000 cfm Cottrells. Average gas velocity is about 3 fps with settling time for suspended solids and water droplets of 17 sec.

Gases entering the conditioning chambers at about 200°F are cooled and humidified by means of high-pressure water sprays to the afore-mentioned conditions. A portion of the run-off water from the conditioning chambers is recirculated after settling of solids in a 30 ft sq settling basin. Warm water makeup is added to enhance vaporization in the conditioning chambers. Bleed-off water, which contains some soluble zinc, is used in the sinter mix.

Water to the conditioner sprays is pressured by a four-stage centrifugal pump operating at 500 psi pressure. High pressure was found desirable in order to obtain effective water vaporization with a reasonable number of sprays.

The material settled in the conditioning chambers, which closely resembles sinter in chemical composition, is cleaned out periodically, allowed to dry by stockpiling a short while, and fed back into the Prime Western sinter mix circuit through a screw feeder. This material represents roughly 1 pct of the calcine and soft sinter feed to the sinter charge.



# The Aging of Sand-Cast Mg-Al-Zn Alloys

by T. E. Leontis and C. E. Nelson

THE properties and casting characteristics of sand-cast Mg-Al-Zn alloys, used commercially in this country and abroad, have been discussed in a number of articles during the past few years.<sup>1-6</sup> In addition, broad surveys of many compositions in the magnesium corner of the Mg-Al-Zn diagram between 0 and 12 pct Al and 0 and 6 pct Zn have been presented by Busk and Marande<sup>7</sup> and by Fox.<sup>8</sup> The purpose of this paper is to furnish a comprehensive survey of the changes in tensile properties, microstructure, and dimensional stability of two magnesium alloys, AZ92A and AZ63A,\* as a function of aging time and temperature after solution heat treatment.

Rates of precipitation in Mg-Al-Zn alloys are slow enough so that a substantially homogeneous, supersaturated solid solution can be maintained even when these alloys are air-cooled from the heat-treating temperature. Consequently, even though it has been demonstrated<sup>9, 10</sup> that significantly higher strengths can be developed in some alloys in the aged condition by quenching rather than air cooling from the heat-treating temperature, general practice is to air-cool magnesium alloys. All the work discussed in this paper is based, therefore, on aging studies performed on material air-cooled from the heat-treating temperature. This investigation was intended to be a study of commercially practical aging cycles; the tensile properties were determined, therefore, up to aging times of 25-hr duration.

The alloys used in this investigation were prepared in the laboratory by remelting commercial ingots of the appropriate composition according to the procedures described in a previous paper<sup>11</sup> as the "crucible method." All melts were given the standard superheating treatment in order to insure the maintenance of a uniform grain size of 0.003 to 0.004 in. Standard test bars, 6½ in. long with a 2½ in. long reduced section having a diameter of ½ in., were cast from these melts in green-sand molds using a four-bar pattern.

The alloys were heat treated according to the following schedules:

AZ92A alloy: 500° to 780°F in 2 hr + 780°F (24 hr)

AZ63A alloy: 500° to 740°F in 2 hr + 740°F (16 hr)

In commercial practice,<sup>12</sup> AZ92A alloy is heat treated at 770°F for 18 hr and AZ63A alloy is heat treated at 730°F for 10 hr. The slightly higher temperatures and longer periods of heat treatment were used in order to obtain as homogeneous a solid solution as possible and thus to minimize inconsistencies in the

data after aging. The preheat is the same as used commercially and is necessary for preventing liquation in segregated areas of nonequilibrium eutectic commonly found in cast Mg-Al-Zn alloys. All heat treatments were performed in circulating air furnaces electrically heated and controlled to  $\pm 5^\circ\text{F}$ . The atmosphere of the furnace was rendered protective by the maintenance of a concentration of 0.5 to 1.0 pct sulphur dioxide. Aging treatments were performed either in the same furnaces but without

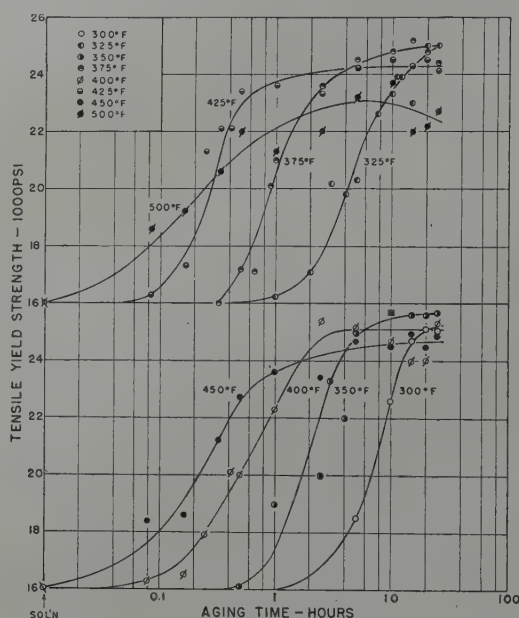


Fig. 1—Tensile yield strength of AZ92A alloy. Temperature legend applies to Figs. 1 to 8.

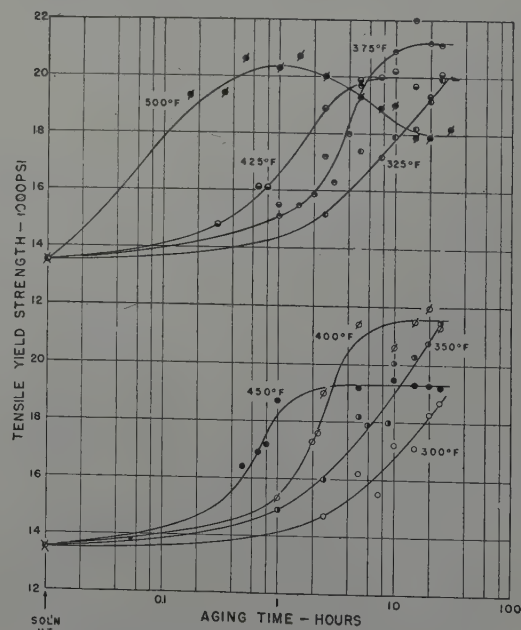


Fig. 2—Tensile yield strength of AZ63A alloy.

\* ASTM designation for magnesium alloys:

AZ92A = Mg + 9Al + 2Zn + 0.2Mn

AZ63A = Mg + 6Al + 3Zn + 0.2Mn

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the use of sulphur dioxide, or in electrically heated oil baths controlled to  $\pm 1^\circ\text{F}$ .

The tensile properties were determined on the cast-to-size test bars without machining the surface. Most of the property values are the average of eight determinations, one bar being taken from each of eight separately cast batches of each alloy. Yield strength values are based on 0.2 pct offset; elongations are over a 2-in. gage length.

The dimensional changes accompanying aging were determined on the same type of cast bars. After solution heat treatment, the shoulders of the bars were machined to a diameter of 0.675 in. and the ends were faced parallel to a length of  $5.7 \pm 0.05$  in. and polished to a fineness of 1/0 grit emery paper. All measurements of length were made with a dial gage mounted on a specially constructed fixture. The smallest division on the gage was 0.0001 in. All measurements were made in a constant-temperature room after the bars had been allowed to stand in the room for at least 1 hr. The actual temperature at the time of measuring was recorded and all length readings were reduced to equivalent lengths at  $80^\circ\text{F}$ .

### Tensile Properties and Hardness

The tensile yield strength, elongation, and hardness of AZ92A and AZ63A alloys are presented as a function of aging time for a series of aging temperatures in Figs. 1 to 6, inclusive.

The tensile strengths have not been plotted in the same way because of the slight change that takes place in this property upon aging. Tensile strength

values for selected aging times at all aging temperatures are given in Table I. The tensile strength of AZ92A does not deviate significantly from the value of 40,000 psi in the solution heat-treated state. The same is true for AZ63A alloy except after extended aging times at the higher aging temperatures.

The aging curves in Figs. 1 to 6 show that these magnesium alloys exhibit a considerable degree of age hardening as measured by the increase in yield strength and hardness and the decrease in ductility with increasing aging time. The curves follow the general S-curve trends observed in all age-hardening alloy systems. Rate of increase in strength and hardness increases with increasing aging temperature and the maximum property decreases with increasing temperature.

The higher alloy content of AZ92A alloy produces a greater rate of aging in this alloy than that exhibited by AZ63A alloy. Also, significantly higher strength and somewhat lower ductility are developed in AZ92A alloy. Although aging of AZ63A alloy at  $300^\circ$  and  $350^\circ\text{F}$  has not been extended in this study to sufficiently long times to produce maximum strength at these temperatures, previous work in our laboratory has shown that yield strengths not significantly greater than those obtained at  $375^\circ$  and  $400^\circ\text{F}$  are produced by aging at the lower temperatures for as long as one month.

### Growth

The growth of the two alloys under consideration was determined over a wide range of aging temperatures. The results are depicted in the form of growth vs. time curves in Figs. 7 and 8; the data on these graphs were obtained on material originally in the solution heat-treated condition. All the curves have the shape characteristics of reactions following a process of nucleation and growth.

As in the case of the property changes accompanying aging, AZ92A alloy exhibits a greater amount and faster rate of growth than AZ63A alloy. Neither

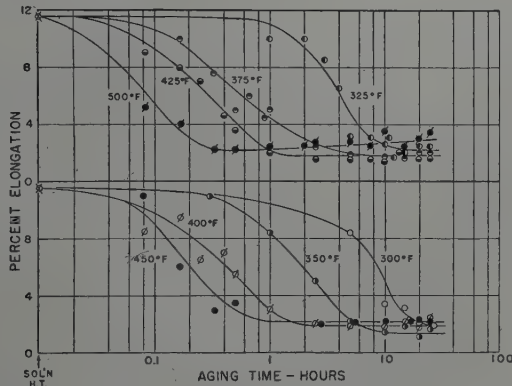


Fig. 3—Elongation of AZ92A alloy.

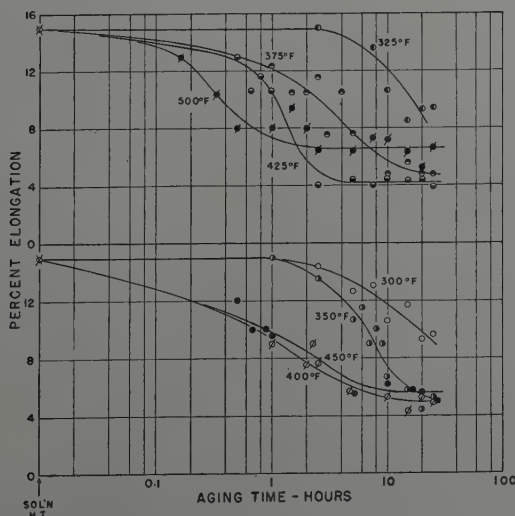


Fig. 4—Elongation of AZ63A alloy.

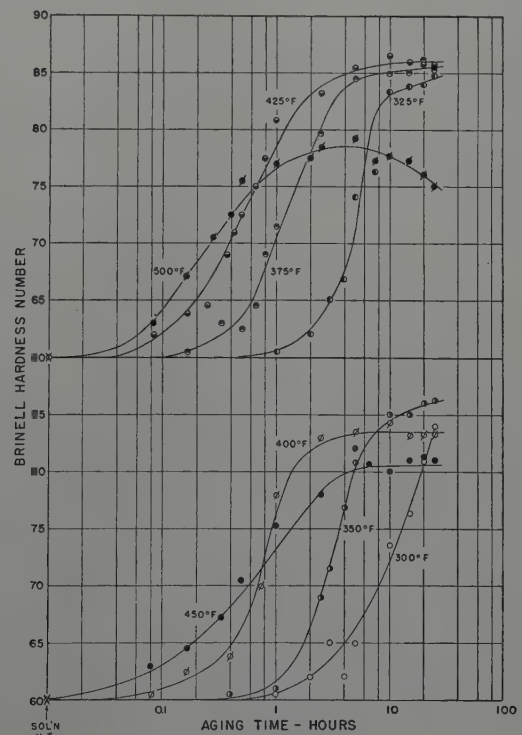


Fig. 5—Brinell hardness of AZ92A alloy.



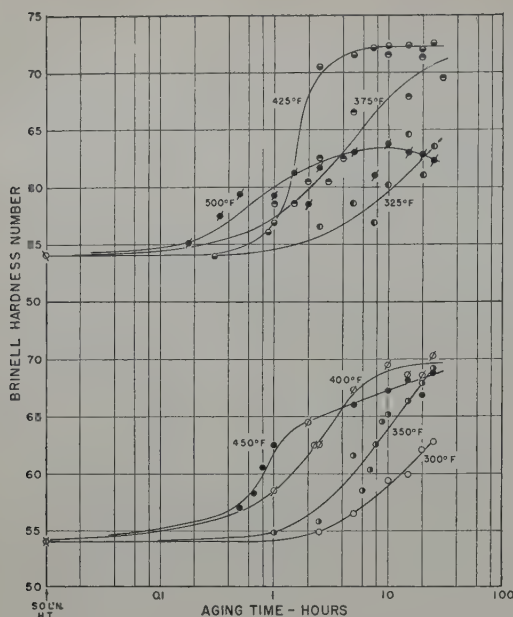


Fig. 6 (left) — Brinell hardness of AZ63A alloy.

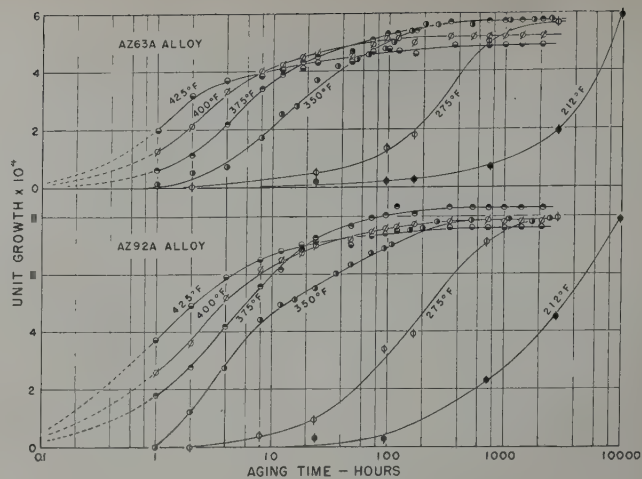


Fig. 7 (above) — Growth of AZ63A and AZ92A alloys.

AZ92A nor AZ63A attains maximum growth at 212°F in 10,000 hr of aging. A few growth measurements have been performed on material in the as-cast condition. The results of these tests, tabulated in Table II, indicate a substantial amount of aluminum and zinc are retained in solid solution when these alloys cool from the freezing temperature. Unfortunately, these measurements have not been carried to sufficiently long aging times to arrive at equilibrium values. Nevertheless, they do indicate that growth is encountered in as-cast material. Fig. 9 shows the variation in the amount of growth with temperature. The marked decrease in growth of both alloys at temperatures above 425°F is closely associated with the rapid increase in solubility of aluminum and zinc in magnesium at these temperatures. These curves also show that the present commercial aging treatment of 5 hr at 425°F is a good selection. This aging cycle contributes nearly maximum strength properties (Figs. 1 and 2) as well as high dimensional stability in as short an aging time as can be obtained. Furthermore, there is considerable advantage in practice in having one aging treatment for both alloys.

Another important consideration in castings is the relief of residual stresses that may be present in the as-cast state or that may arise from cooling after

heat treatment. It has been determined by Found and Pittsley<sup>13</sup> that the magnitude of residual stresses in magnesium-alloy castings is considerably lower than that generally encountered in other alloys. The work of these investigators also shows that stresses arising in AZ63A and AZ92A alloys in cooling from the heat-treating temperature are essentially eliminated by the aging treatment recommended in the present paper.

The time required to attain a certain percentage of the maximum possible growth at each temperature is a measure of the rate of precipitation at that temperature. A linear relation should exist between the logarithm of this time quantity and the reciprocal of the absolute temperature. Such a plot is shown in Fig. 10. Deviations from the linear relationship are exhibited by both alloys at the higher temperatures. The marked increase in the solid solubility of the alloying elements in magnesium at temperatures greater than 450°F decreases the driving force of the precipitation reaction at these temperatures. The effect is naturally more pronounced in the alloy of lower total alloy content.

### Microstructure

In Figs. 11 and 12 are shown selected microstructures of AZ92A and AZ63A alloys after various degrees of aging. The structures of the alloys in the

Table I. Tensile Strength as a Function of Aging Temperature and Time

| Aging Temp, °F     | Tensile Strength (1000 psi) for Indicated Aging Time, Hr |      |      |      |      |      |      |
|--------------------|----------------------------------------------------------|------|------|------|------|------|------|
|                    | 1                                                        | 2½   | 5    | 10   | 15   | 20   | 25   |
| <b>AZ92A Alloy</b> |                                                          |      |      |      |      |      |      |
| 300                |                                                          |      | 42.6 | 40.6 | 44.3 | 43.1 | 42.6 |
| 325                | 40.6                                                     | 42.6 | 41.7 | 42.6 | 43.1 | 43.7 | 43.8 |
| 350                | 42.0                                                     | 41.3 | 43.2 | 42.4 | 42.7 | 41.4 | 43.2 |
| 375                | 42.8                                                     | 42.0 | 42.7 | 40.4 | 40.5 | 41.2 | 42.0 |
| 400                | 40.4                                                     | 44.0 | 41.5 | 41.6 | 42.3 | 41.2 | 42.1 |
| 425                |                                                          | 40.7 | 39.2 | 40.0 | 39.7 | 39.3 | 40.0 |
| 450                | 37.8                                                     | 41.6 | 41.0 | 39.9 | 40.9 | 39.5 | 39.9 |
| 500                | 37.8                                                     | 41.4 | 40.9 | 41.6 | 38.0 | 39.1 | 39.3 |
| <b>AZ63A Alloy</b> |                                                          |      |      |      |      |      |      |
| 300                |                                                          | 41.6 | 39.9 | 40.1 | 41.1 | 40.2 | 41.4 |
| 325                |                                                          | 41.5 | 41.5 | 41.4 | 41.7 | 41.0 | 42.9 |
| 350                | 42.2                                                     | 42.8 | 42.9 | 40.1 | 41.1 | 40.1 | 37.4 |
| 375                | 42.4                                                     | 44.5 | 40.9 | 39.8 | 39.5 | 39.3 | 38.5 |
| 400                | 41.4                                                     | 43.8 | 38.2 | 39.6 | 37.0 | 38.7 | 39.5 |
| 425                | 41.3                                                     | 39.1 | 39.3 | 40.2 | 39.6 | 39.1 | 38.7 |
| 450                | 43.3                                                     | 39.6 | 37.7 | 38.4 | 38.4 | 37.9 | 37.6 |
| 500                |                                                          | 39.8 | 38.4 | 37.3 | 37.4 | 35.8 | 37.2 |

Table II. Growth Upon Aging Alloys in the As-Cast Condition

| Alloy | Aging Temp, °F | Unit Growth, Aging Time, Hr |         |         |         |
|-------|----------------|-----------------------------|---------|---------|---------|
|       |                | 24                          | 96      | 168     | 720     |
| AZ92A | 275            | 0.00008                     | 0.00014 | 0.00014 | 0.00034 |
|       | 350            | 0.00022                     | 0.00029 | 0.00031 | 0.00034 |
| AZ63A | 275            | 0.00001                     | 0.00014 | 0.00012 | 0.00025 |
|       | 350            | 0.00013                     | 0.00025 | 0.00025 | 0.00026 |

Table III. Increase in Tensile Strength and Ductility

| As-Cast   |          |      |                      | Solution Heat Treated |          |      |                      |
|-----------|----------|------|----------------------|-----------------------|----------|------|----------------------|
| E, Pct    | 1000 Psi |      | Brinell Hardness No. | E, Pct                | 1000 Psi |      | Brinell Hardness No. |
|           | TYS      | TS   |                      |                       | TYS      | TS   |                      |
| AZ92A 1.6 | 15.7     | 25.0 | 62                   | 11.6                  | 16.0     | 41.5 | 60                   |
| AZ63A 7.0 | 14.0     | 30.9 | 57                   | 15.0                  | 13.5     | 40.6 | 54                   |



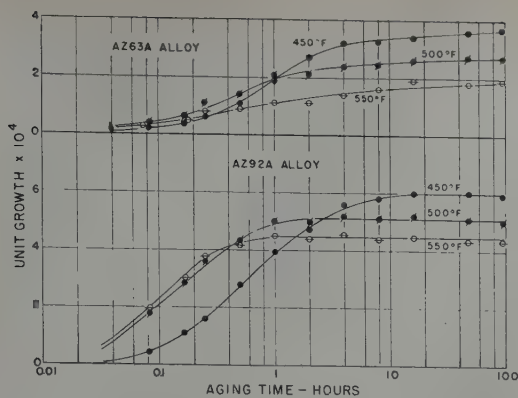
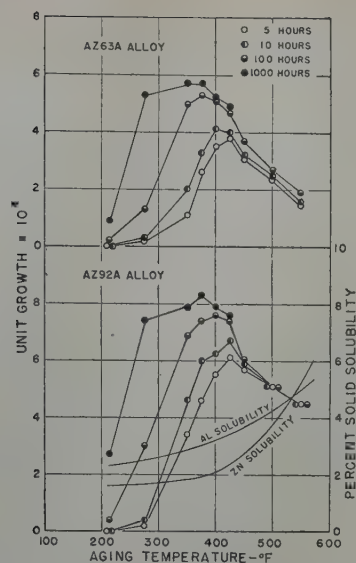


Fig. 8 (above)—Growth of AZ63A and AZ92A alloys. These data supplement those in Fig. 7.

Fig. 9 (right)—Growth vs. temperature.



solution heat-treated condition is not shown inasmuch as they have appeared in the previous publications.<sup>10, 14</sup> This solution treatment dissolves the  $Mg_{17}Al_{12}$  compound in the magnesium phase but leaves small particles of Mn and  $Mg_2Si$  undissolved. Solution heat treatment produces an increase in tensile strength and ductility as shown in Table III.

The structures shown in the accompanying figures illustrate that there are two distinct types of precipitate in the aged condition of Mg-Al-Zn alloys. One is the discontinuous type which forms at the grain boundaries and resembles pearlite in appearance. The other is the continuous type which appears within the grains and forms a Widmanstätten pattern.

In the temperature range investigated, the first precipitate to form is the pearlitic type along the grain boundaries. As aging proceeds, a finely divided precipitate appears within the grains, usually beginning at the center of each grain and proceeding outward to the grain-boundary precipitate. The discontinuous precipitate consists of alternate plates of  $Mg_{17}Al_{12}$  and Mg solid solution. The higher the temperature, the greater is the lamellar spacing of the pearlitic precipitate. At a magnification of 250X, the lamellae are not resolved in either alloy aged at temperatures below 425°F. In the micrographs presented here, the true nature of this pearlitic precipitate can be seen only in AZ63A alloy aged at 500°F (Fig. 12f). In structures produced in AZ92A alloy by aging at temperatures above 425°F, it is difficult to distinguish the two types of precipitate (Fig. 11f).

The more rapid rate of aging of AZ92A alloy is again demonstrated by the micrographs. As an example, comparison of Figs. 11b with 12a shows that after the same aging treatment, AZ92A alloy has

considerably more precipitate than AZ63A. Similar comparisons can be made for other aging treatments.

### Summary

The aging studies on two commercial Mg-Al-Zn alloys, AZ63A and AZ92A, reported in this paper show that a wide variation in the properties can be attained by selection of aging temperature and time. Properties typical of these two alloys in the fully aged condition are given in Table IV.

Although both AZ63A and AZ92A alloys exhibit a measurable amount of growth when aged after solution heat treatment, suitable aging treatments render these alloys dimensionally stable to subsequent exposure at temperatures prevailing in engine applications. The figures in Table V indicate the maximum possible growth that can be expected in AZ63A and AZ92A alloys in the heat-treated and in

Table IV. Typical Properties of Fully Aged AZ92A and AZ63A

|       | E, Pct | 1000 Psi |    | BHN |
|-------|--------|----------|----|-----|
|       |        | TYS      | TS |     |
| AZ92A | 2      | 23       | 40 | 84  |
| AZ63A | 5      | 19       | 40 | 73  |

Table V. Maximum Possible Growth of AZ92A and AZ63A

|       | Maximum Possible Unit Growth |                     |
|-------|------------------------------|---------------------|
|       | Solution Heat Treated        | Heat Treated + Aged |
| AZ92A | 0.00083                      | 0.00022             |
| AZ63A | 0.00059                      | 0.00021             |

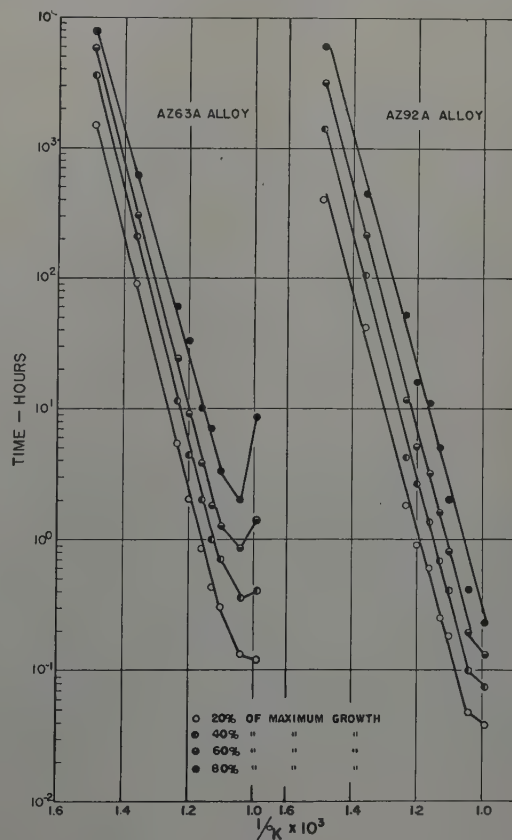


Fig. 10—Time for constant percent of maximum growth vs.  $1/T$ .



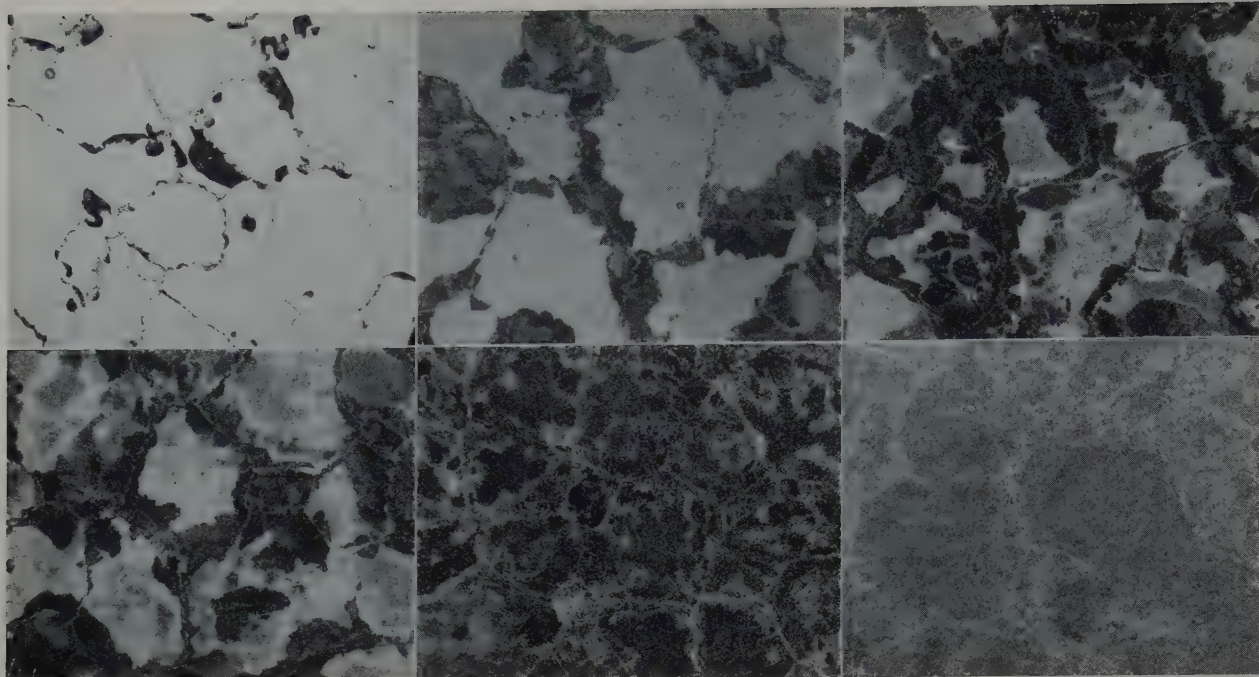


Fig. 11—Microstructure of AZ92A alloy, solution heat treated and aged.  
Acetic glycol etchant. X250. Area reduced approximately 50 pct for reproduction.  
a (upper left)—Aged at 300°F, 5 hr. b (upper center)—Aged at 300°F, 25 hr.  
c (upper right)—Aged at 350°F, 15 hr. d (lower left)—Aged at 375°F, 15 hr.  
e (lower center)—Aged at 425°F, 5 hr. f (lower right)—Aged at 500°F, 5 hr.

the heat-treated and aged condition. The satisfactory performance of these alloys in engine parts during the past years indicates that remaining possible growth after aging is of little consequence.

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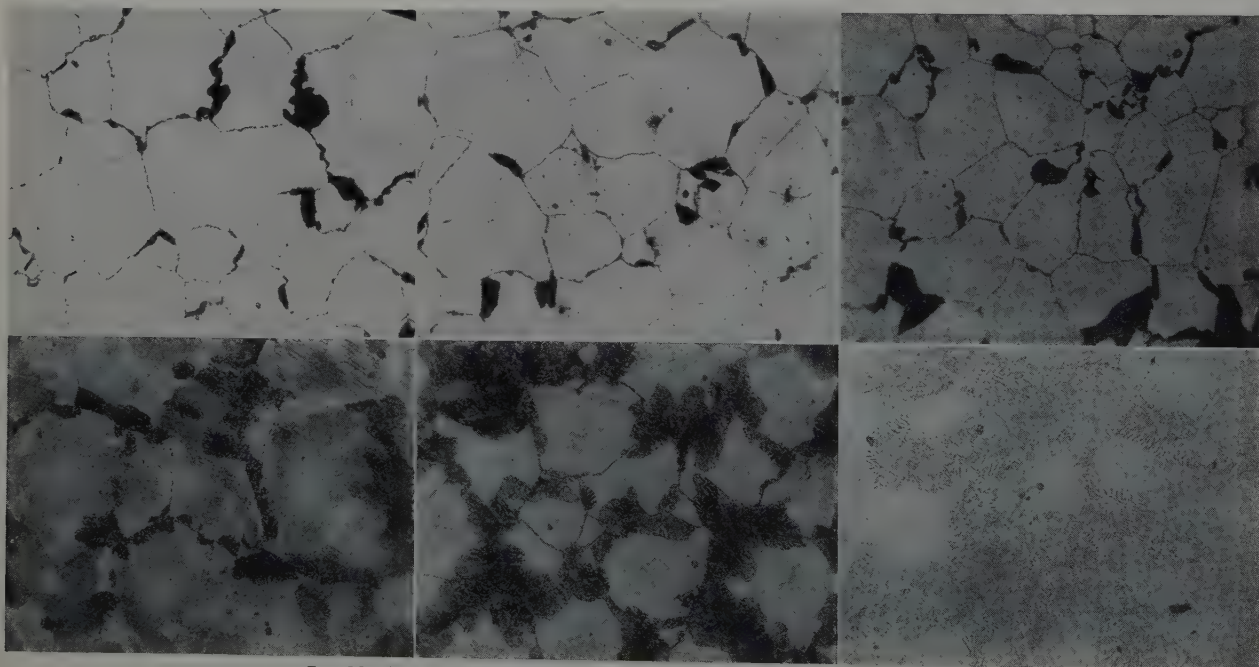


Fig. 12—Microstructure of AZ63A alloy, solution heat treated and aged.  
Acetic glycol etchant. X250. Area reduced approximately 50 pct for reproduction.  
a (upper left)—Aged at 300°F, 25 hr. b (upper center)—Aged at 350°F, 5 hr.  
c (upper right)—Aged at 350°F, 15 hr. d (lower left)—Aged at 375°F, 15 hr.  
e (lower center)—Aged at 425°F, 5 hr. f (lower right)—Aged at 500°F, 5 hr.



# Mechanical Properties of Stainless Steel Powder

by

Arthur H. Grobe

and

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**Tensile, hardness and density properties are presented for a new 18-8 stainless steel powder for the —50, —100, and —140 mesh cuts and also for a prepared blend containing 62 pct —325 mesh powder. The data were obtained for sintering temperatures of 2100° to 2350°F and for compacting pressures of 30 to 50 tons per sq in.**

A NEED has existed for a stainless steel powder of uniform composition from particle to particle, which could be readily molded and sintered, and which would yield moderate to high strength and ductility when processed into parts by standard powder metallurgy techniques. The literature reveals that previously available powders have been lacking in one or several of these desirable characteristics. Originally attempts to produce stainless steel powder by blending and diffusing elemental metal powders were unsuccessful.<sup>1</sup> A truly alloyed stainless steel powder reported by Dale in 1947 yielded reasonable mechanical properties but required an exceptionally high sintering temperature of 2400°F in pure dry hydrogen.<sup>1</sup> A later development reported in 1950 by Stern provided a stainless type powder of excellent molding properties<sup>2</sup> but this powder likewise required sintering at temperatures over 2350°F and did not yield properties as high as those previously reported. The powder was not truly alloyed prior to sintering.

A prealloyed stainless steel powder has been developed that is readily moldable at 30 to 50 tons per sq in., can be sintered at low temperatures

(2100° to 2300°F), and which yields compacts with both high strength and ductility. The powder is prepared by the liquid disintegration method,<sup>3</sup> direct from molten metal. Early attempts to make 18 pct Cr, 8 pct Ni stainless steel powder by this method did not produce a usable powder for pressing and sintering because of a preponderance of spherical particles with relatively high, surface oxide content. It was learned that silicon additions to iron alloys, powdered by this process, gave bright powder of low-oxide content and such additions were made to 18-8 stainless with similar results. An attendant change in particle shape occurred reducing the number of spheroids materially. The optimum composition which has been studied and is reported here contains approximately 2.5 pct Si. Silicon additions to stainless steel of the 18-8 type improve the resistance to high-temperature oxidation and promote the formation of ferrite. Corrosion resistance is, however, controlled by chromium content and even though ferrite may exist the corrosion resistance is not generally impaired.<sup>4</sup>

## Experimental Procedure

A detailed study of the 18-8, 2.5 pct Si powder has been made in accordance with the following outline:

1. Four blends
  - a. — 50 mesh
  - b. —100 mesh

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- c. —140 mesh
- d. —100 mesh special mixture with 62 pct —325 mesh

## 2. Properties of powder blends

- a. Apparent density
- b. Flow rate
- c. Compression ratio

## 3. Pressing and sintering

Density, shrinkage and mechanical properties

### a. All blends sintered (sintering time 45 min)

- 1) Pressures—30, 40, 50 tons per sq in.
- 2) Temperatures—2100°, 2200°, 2300°F

### b. All blends sintered—coined\*—resintered (both sintering times 45 min)

- 1) Pressures—30, 40, 50 tons per sq in.
- 2) Temperatures—2100°, 2200°, 2300°F

### c. —100 mesh blend sintered (sintering temperature 2250°F)

- 1) Pressure—30, 40, 50 tons per sq in.
- 2) Times of sintering—15, 45, 90, 180, 300 min

### d. —100 mesh blend sintered—coined (sintering temperatures 2250°F)

- 1) Pressures—30, 40, 50 tons per sq in.
- 2) Times of sintering—15, 45, 90, 180, 300 min

### e. —100 mesh blend sintered—coined—resintered (sintering temperature 2250°F)

- 1) Pressures—30, 40, 50 tons per sq in.
- 2) Times of sintering—15, 45, 90, 130, 300 min

## 4. Properties of wrought material of same composition

Apparent density was determined using the Hall flowmeter with the 25 cc cup. Flow rate was determined in accordance with Metal Powder Association Standard 3-45T. Compression ratio is calculated as the ratio of the green to the apparent density.

Density of pressed and sintered compacts was measured on specimens ½ in. in diam and weighing 12 g. Tensile bars were made in a split die producing

\* All coining pressures the same as original pressing pressure.

Table I. Apparent Density, Flow Rate, Compression Ratios and Sieve Analyses of the Four Blends

| Properties                         | Blends    |           |           |                         |
|------------------------------------|-----------|-----------|-----------|-------------------------|
|                                    | —50 Mesh  | —100 Mesh | —140 Mesh | —100 Mesh with 62% —325 |
| Apparent density, g per cc         | 2.94      | 2.87      | 2.83      | 2.94                    |
| Flow rate, seconds                 | 31.6      | 28.0      | 26.5      | 25.0                    |
| Compression ratio, tons per sq in. | 1.79      | 1.79      | 1.77      | 1.74                    |
|                                    | 1.91      | 1.91      | 1.94      | 1.86                    |
|                                    | 2.01      | 2.01      | 2.04      | 1.96                    |
| Sieve analyses, pct                | +50       | 2.1       |           |                         |
|                                    | —50 +100  | 35.6      | 1.9       |                         |
|                                    | —100 +140 | 17.5      | 24.4      | 5                       |
|                                    | —140 +200 | 13.8      | 23.5      | 10                      |
|                                    | —200 +270 | 11.1      | 13.9      | 8                       |
|                                    | —270 +325 | 5.5       | 14.6      | 15                      |
|                                    | —325      | 14.4      | 21.7      | 62                      |

a square-ended specimen 4 in. x ¼ in. thick. The width at each end was ⅜ in. with a reduced center section ¼ in. wide to provide a gage length of 1 in. All compacts were pressed in a die lubricated with calcium stearate dissolved in carbon tetrachloride. Coining was performed in the same dies, and accordingly some difficulty was encountered in completely coining samples which had exhibited large amounts of shrinkage during the initial sintering.

Sintering was conducted in a tube furnace with a hydrogen atmosphere. Tank hydrogen was deoxidized with platinized alumina and dried in an Electro-dryer. Samples reached the sintering temperature in 15 to 20 min and all sintering times reported are times at temperature. Cooling was accomplished in the same atmosphere in the water-cooled end of the tube, where the samples were held for 30 min.

All samples were measured and weighed before and after each treatment. Shrinkage is recorded as the change in length of the 4-in. tensile specimens. Rockwell F hardness, tensile strength, and elongation values were determined for all treatments on the tensile samples.

A 30-lb induction heat was produced of the same

Table II. Properties of the —50 Mesh Powder

| Compacting and Coining Pressure, Tons per sq in. | Sintering* Temp., °F | Tensile Strength, Psi | Elongation, Pct in 1 in. | Hardness, Rockwell F | Green Density, g per cc | Density After First Sinter, g per cc | Coining Density, g per cc | Density After Final Sinter, g per cc | Shrinkage† During First Sinter, Pct | Shrinkage† During Second Sinter, Pct |
|--------------------------------------------------|----------------------|-----------------------|--------------------------|----------------------|-------------------------|--------------------------------------|---------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 30-0                                             | 2100                 | 9,500                 | 2‡                       | 27.4                 |                         |                                      |                           |                                      |                                     |                                      |
| 30-30                                            | 2100                 | 24,500                | 6‡                       | 64.7                 | 5.26                    | 5.27                                 | 5.80                      | 5.80                                 | 0.4                                 |                                      |
| 40-0                                             | 2100                 | 15,500                | 2                        | 52.1                 |                         |                                      |                           |                                      | 0.4                                 |                                      |
| 40-40                                            | 2100                 | 33,000                | 8                        | 76.3                 | 5.63                    | 5.65                                 | 6.24                      | 6.25                                 | 0.3                                 | 0.1                                  |
| 50-0                                             | 2100                 | 13,000                | 2                        | 68.8                 |                         |                                      |                           |                                      | 0.3                                 |                                      |
| 50-50                                            | 2100                 | 42,000                | 8                        | 78.9                 | 5.88                    | 5.90                                 | 6.58                      | 6.58                                 | 0.3                                 | 0.1                                  |
| 30-0                                             | 2200                 | 15,000                | 4‡                       | 39.4                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 30-30                                            | 2200                 | 37,000                | 12                       | 68.9                 | 5.23                    | 5.35                                 | 5.87                      | 5.94                                 | 0.5                                 | 0.3                                  |
| 40-0                                             | 2200                 | 20,500                | 5                        | 59.5                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 40-40                                            | 2200                 | 45,500                | 16                       | 82.0                 | 5.57                    | 5.67                                 | 6.31                      | 6.36                                 | 0.4                                 | 0.2                                  |
| 50-0                                             | 2200                 | 28,000                | 8                        | 69.0                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 50-50                                            | 2200                 | 60,500                | 22                       | 85.5                 | 5.82                    | 5.91                                 | 6.56                      | 6.60                                 | 0.5                                 | 0.3                                  |
| 30-0                                             | 2300                 | 27,500                | 8‡                       | 51.4                 |                         |                                      |                           |                                      | 1.2                                 |                                      |
| 30-30                                            | 2300                 | 46,500                | 13                       | 82.9                 | 5.30                    | 5.55                                 | 5.83                      | 6.04                                 | 1.2                                 | 1.2                                  |
| 40-0                                             | 2300                 | 31,000                | 9                        | 65.2                 |                         |                                      |                           |                                      | 1.0                                 |                                      |
| 40-40                                            | 2300                 | 70,000                | 25                       | 88.0                 | 5.68                    | 5.90                                 | 6.23                      | 6.49                                 | 1.0                                 | 1.1                                  |
| 50-0                                             | 2300                 | 32,500                | 8                        | 74.3                 |                         |                                      |                           |                                      | 1.0                                 |                                      |
| 50-50                                            | 2300                 | 80,000                | 27                       | 91.8                 | 6.01                    | 6.24                                 | 6.55                      | 6.81                                 | 1.1                                 | 0.9                                  |

\* Sintering time was 45 min at temperature.

† Shrinkage was measured on the 4 in. length of the tensile specimen.

‡ Specimen broke beyond gage marks.



Table III. Properties of —100 Mesh Powder

| Compacting and Coining Pressure, Tons per sq in. | Sintering* Temp., °F | Tensile Strength, Psi | Elongation, Pct in 1 in. | Hardness, Rockwell F | Green Density, g per cc | Density After First Sinter, g per cc | Coining Density, g per cc | Density After Final Sinter, g per cc | Shrinkage† During First Sinter, Pct | Shrinkage† During Second Sinter, Pct |
|--------------------------------------------------|----------------------|-----------------------|--------------------------|----------------------|-------------------------|--------------------------------------|---------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 30-0                                             | 2100                 | 15,000                | 4                        | 43.0                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 30-30                                            | 2100                 | 31,000                | 10‡                      | 57.3                 | 5.13                    | 5.20                                 | 5.68                      | 5.68                                 | 0.6                                 | 0.1                                  |
| 40-0                                             | 2100                 | 20,000                | 3‡                       | 48.8                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 40-40                                            | 2100                 | 44,500                | 15‡                      | 76.3                 | 5.50                    | 5.58                                 | 6.08                      | 6.10                                 | 0.5                                 | 0.1                                  |
| 50-0                                             | 2100                 | 26,000                | 6                        | 66.0                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 50-50                                            | 2100                 | 49,000                | 17                       | 81.2                 | 5.79                    | 5.86                                 | 6.43                      | 6.43                                 | 0.5                                 | 0.1                                  |
| 30-0                                             | 2200                 | 20,500                | 10                       | 48.4                 |                         |                                      |                           |                                      | 0.8                                 |                                      |
| 30-30                                            | 2200                 | 40,500                | 13                       | 64.3                 | 5.15                    | 5.30                                 | 5.71                      | 5.84                                 | 0.8                                 | 0.7                                  |
| 40-0                                             | 2200                 | 25,500                | 8                        | 54.7                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 40-40                                            | 2200                 | 54,000                | 20                       | 78.7                 | 5.48                    | 5.59                                 | 6.14                      | 6.23                                 | 0.7                                 | 0.4                                  |
| 50-0                                             | 2200                 | 29,500                | 9‡                       | 61.1                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 50-50                                            | 2200                 | 63,500                | 22                       | 86.2                 | 5.76                    | 5.88                                 | 6.44                      | 6.53                                 | 0.6                                 | 0.4                                  |
| 30-0                                             | 2300                 | 32,500                | 13                       | 56.8                 |                         |                                      |                           |                                      | 2.0                                 |                                      |
| 30-30                                            | 2300                 | 52,000                | 15                       | 78.5                 | 5.12                    | 5.59                                 | 5.76                      | 6.16                                 | 2.2                                 | 1.8                                  |
| 40-0                                             | 2300                 | 41,500                | 15                       | 73.8                 |                         |                                      |                           |                                      | 1.9                                 |                                      |
| 40-40                                            | 2300                 | 74,500                | 26                       | 85.2                 | 5.44                    | 5.90                                 | 6.12                      | 6.49                                 | 2.0                                 | 1.7                                  |
| 50-0                                             | 2300                 | 49,000                | 17                       | 76.7                 |                         |                                      |                           |                                      | 1.7                                 |                                      |
| 50-50                                            | 2300                 | 87,000                | 32                       | 91.0                 | 5.75                    | 6.19                                 | 6.43                      | 6.79                                 | 1.8                                 | 1.5                                  |
| 40-40                                            | 2350                 | 78,000                | 28                       | 97.2                 | 5.47                    | 6.15                                 |                           |                                      | 3.1                                 | 1.6                                  |
| 50-50                                            | 2350                 | 78,500                | 26‡                      | 103.4                | 5.71                    | 6.31                                 |                           |                                      | 2.4                                 | 1.4                                  |

\* Sintering time was 45 min at temperature.

† Shrinkage was measured on the 4 in. length of the tensile specimen.

‡ Specimen broke beyond gage marks.

composition and forged from a 3-in. ingot to a  $\frac{7}{8}$  in. sq bar. Tensile specimens were machined of the same size and design as those employed for the powder compacts.

### Experimental Results

The powder employed was of the following composition: C, 0.09 pct; Si, 2.42; Mn, 0.63; S, 0.007; P, 0.019; Cr, 17.48; and Ni, 8.02.

All of the blends tested molded very well. For commercial applications the —50 mesh powder would yield best moldability at 40 to 50 tons. Standard —100 mesh powder is equivalent to this at 40 tons, while the finer powders have commercially satisfactory green strength at 30 tons.

The basic powder properties and the sieve analyses

of the four blends are shown in Table I. This is fundamentally a free flowing powder in all blends with an apparent density of approximately 2.9 g per cc.

Tables II to V, inclusive, present the complete property information for the four blends or cuts studied when pressed at 30 to 50 tons per sq in. and sintered for 45 min at 2100° to 2300°F. In the first column the figures "30-0", for example, indicate pressing-sintering-coining and resintering.

There is a general tendency for the tensile strength and elongation to increase slightly as the particle size decreases. This is especially pronounced at low densities. On the other hand, shrinkage increases greatly as the average particle size becomes finer.

Table IV. Properties of —140 Mesh Powder

| Compacting and Coining Pressure, Tons per sq in. | Sintering* Temp., °F | Tensile Strength, Psi | Elongation, Pct in 1 in. | Hardness, Rockwell F | Green Density, g per cc | Density After First Sinter, g per cc | Coining Density, g per cc | Density After Final Sinter, g per cc | Shrinkage† During First Sinter, Pct | Shrinkage† During Second Sinter, Pct |
|--------------------------------------------------|----------------------|-----------------------|--------------------------|----------------------|-------------------------|--------------------------------------|---------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 30-0                                             | 2100                 | 17,000                | 3‡                       | 38.0                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 30-30                                            | 2100                 | 31,000                | 12                       | 66.7                 | 5.10                    | 5.19                                 | 5.63                      | 5.64                                 | 0.6                                 | 0.2                                  |
| 40-0                                             | 2100                 | 21,000                | 4‡                       | 61.0                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 40-40                                            | 2100                 | 39,000                | 13                       | 73.2                 | 5.51                    | 5.59                                 | 6.14                      | 6.15                                 | 0.5                                 | 0.1                                  |
| 50-0                                             | 2100                 | 27,000                | 6‡                       | 60.9                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 50-50                                            | 2100                 | 50,500                | 17                       | 84.9                 | 5.77                    | 5.87                                 | 6.43                      | 6.44                                 | 0.5                                 | 0.1                                  |
| 30-0                                             | 2200                 | 21,000                | 10                       | 38.8                 |                         |                                      |                           |                                      | 0.8                                 |                                      |
| 30-30                                            | 2200                 | 40,000                | 15                       | 68.3                 | 5.11                    | 5.29                                 | 5.61                      | 5.79                                 | 0.8                                 | 0.6                                  |
| 40-0                                             | 2200                 | 26,000                | 6                        | 61.7                 |                         |                                      |                           |                                      | 0.8                                 |                                      |
| 40-40                                            | 2200                 | 52,000                | 18                       | 78.2                 | 5.49                    | 5.64                                 | 6.13                      | 6.24                                 | 0.9                                 | 0.5                                  |
| 50-0                                             | 2200                 | 33,500                | 10‡                      | 70.2                 |                         |                                      |                           |                                      | 0.7                                 |                                      |
| 50-50                                            | 2200                 | 60,000                | 21                       | 85.7                 | 5.78                    | 5.92                                 | 6.43                      | 6.54                                 | 0.7                                 | 0.3                                  |
| 30-0                                             | 2300                 | 38,500                | 14                       | 63.8                 |                         |                                      |                           |                                      | 2.8                                 |                                      |
| 30-30                                            | 2300                 | 59,500                | 20                       | 83.0                 | 5.08                    | 5.73                                 | 5.86                      | 6.29                                 | 2.8                                 | 1.8                                  |
| 40-0                                             | 2300                 | 42,000                | 14                       | 67.2                 |                         |                                      |                           |                                      | 2.1                                 |                                      |
| 40-40                                            | 2300                 | 70,000                | 24                       | 89.8                 | 5.50                    | 6.06                                 | 6.27                      | 6.69                                 | 2.1                                 | 1.7                                  |
| 50-0                                             | 2300                 | 50,500                | 17                       | 80.4                 |                         |                                      |                           |                                      | 2.0                                 |                                      |
| 50-50                                            | 2300                 | 80,500                | 27                       | 94.8                 | 5.78                    | 6.32                                 | 6.56                      | 6.91                                 | 2.1                                 | 1.5                                  |
| 40-40                                            | 2350                 | 84,500                | 30                       | 103.3                | 5.45                    | 6.28                                 |                           |                                      | 3.8                                 | 1.8                                  |
| 50-50                                            | 2350                 | 86,000                | 31                       | 107.1                | 5.73                    | 6.48                                 |                           |                                      | 2.9                                 | 1.6                                  |

\* Sintering time was 45 min at temperature.

† Shrinkage was measured on the 4 in. length of the tensile specimen.

‡ Specimen broke beyond gage marks.



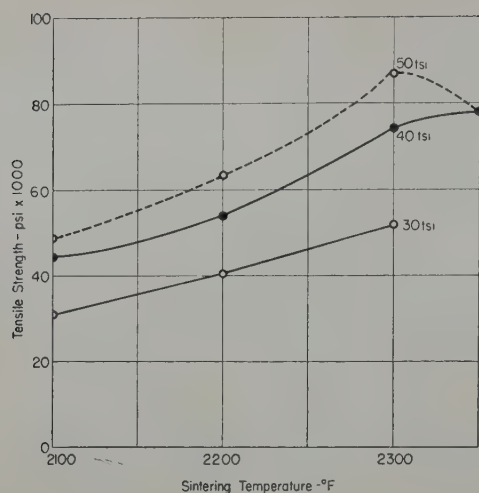


Fig. 1—Tensile strength vs. sintering temperature for —100 mesh powder.  
Sintered, coined, and resintered. Each sintering 45 min at temperature. Pressed and coined at pressures shown.

For commercial applications a shrinkage of 1 to 1.4 pct is practical, and accordingly —50 mesh powder could be sintered at 2300°F for 45 min while the very finest powder tested should be sintered at 2200°F if shrinkage is the prime consideration.

The detailed study made of the —100 mesh powder sintered at 2250°F was predicated on the shrinkage consideration which indicated this temperature as optimum for the powder. Data shown in Table VI record all properties obtained by varying the sintering time from 15 to 300 min and the pressing and coining pressures from 30 to 50 tons per sq in. In this instance tensile tests were made on bars sintered and coined with no subsequent resintering in addition to the usual conditions in which sintering was the final operation. It is to be particularly noted that while the tensile strength is increased by coining, the elongation is reduced markedly. Nevertheless, elongations still remain at a relatively high level for powder parts. One factor not recorded in these data is the great increase in yield strength that is a

natural result of the coining operation and is of engineering importance.

Selected information from the tables has been assembled into graph form in Fig. 1 to show the trends of properties as a function of the major commercial variables for the standard —100 mesh powder.

The tensile strength of —100 mesh powder increases approximately 100 pct as the sintering temperature is increased from 2100° to 2300°F. A consistent but smaller improvement results from increasing the pressure from 30 to 50 tons per sq in. These results apply to single pressing and sintering. Fig. 1 refers to these same variables but after coining and resintering. The properties after the treatment at 2100°F are equal to those of single sintering at 2300°F. Values of tensile strength over 80,000 psi are obtained at 2300°F with a pressing and coining pressure of 50 tons per sq in.

The increase in strength by lengthening the sintering time beyond 1 hr is slight, but the increase from 15 to 45 min is significant. The increased tensile strength as a result of coining without resintering is apparent.

The tabular shrinkage data are not as consistent as would be obtained commercially, since each specimen in this entire series of tests was individually pressed and sintered, thus increasing the difficulty of obtaining precise control.

From the tabular data it is apparent that the tensile strength and elongation increase simultaneously and in a regular manner except for those samples on which the final operation was coining. In Fig. 2 the validity of this relationship is established. Open circles are plotted for each and every tensile specimen broken, regardless of screen size, pressing, or sintering conditions. The curve is a straight line until tensile strengths of 85,000 psi are reached, when the elongation increases at a more rapid rate. This is caused by the close approach of the tensile strength to that of the wrought material, whereas the elongation is still considerably lower than that of the wrought material. Coined samples show a lower elongation and a poorer correlation than sintered samples (see solid circles in Fig. 2).

Table V. Properties of —100 Mesh Powder with 62 Pct —325 Mesh

| Compacting and Coining Pressure, Tons per sq in. | Sintering* Temp., °F | Tensile Strength, Psi | Elongation, Pct in 1 in. | Hardness, Rockwell, F | Green Density, g per cc | Density After First Sinter, g per cc | Coined Density, g per cc | Density After Final Sinter, g per cc | Shrinkage† During First Sinter, Pct | Shrinkage‡ During Second Sinter, Pct |
|--------------------------------------------------|----------------------|-----------------------|--------------------------|-----------------------|-------------------------|--------------------------------------|--------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 30-0                                             | 2100                 | 20,000                | 7                        | 46.1                  |                         |                                      |                          |                                      | 0.8                                 |                                      |
| 30-30                                            | 2100                 | 33,500                | 13                       | 67.7                  | 5.13                    | 5.25                                 | 5.69                     | 5.72                                 | 0.8                                 | 0.3                                  |
| 40-0                                             | 2100                 | 26,000                | 9                        | 60.0                  |                         |                                      |                          |                                      | 0.8                                 |                                      |
| 40-40                                            | 2100                 | 44,000                | 16                       | 78.3                  | 5.47                    | 5.60                                 | 6.07                     | 6.10                                 | 0.8                                 | 0.2                                  |
| 50-0                                             | 2100                 | 31,500                | 7‡                       | 72.5                  |                         |                                      |                          |                                      | 0.7                                 |                                      |
| 50-50                                            | 2100                 | 50,000                | 14                       | 84.5                  | 5.74                    | 5.85                                 | 6.38                     | 6.40                                 | 0.7                                 | 0.2                                  |
| 30-0                                             | 2200                 | 24,000                | 10                       | 53.5                  |                         |                                      |                          |                                      | 1.3                                 |                                      |
| 30-30                                            | 2200                 | 42,000                | 15                       | 68.7                  | 5.14                    | 5.46                                 | 5.72                     | 6.00                                 | 1.3                                 | 0.8                                  |
| 40-0                                             | 2200                 | 30,000                | 10                       | 61.8                  |                         |                                      |                          |                                      | 1.1                                 |                                      |
| 40-40                                            | 2200                 | 53,000                | 18                       | 82.1                  | 5.45                    | 5.73                                 | 6.06                     | 6.30                                 | 1.1                                 | 0.7                                  |
| 50-0                                             | 2200                 | 36,500                | 12                       | 70.1                  |                         |                                      |                          |                                      | 1.0                                 |                                      |
| 50-50                                            | 2200                 | 60,000                | 18                       | 84.5                  | 5.77                    | 6.04                                 | 6.37                     | 6.57                                 | 1.0                                 | 0.4                                  |
| 30-0                                             | 2300                 | 43,500                | 14‡                      | 70.4                  |                         |                                      |                          |                                      | 3.8                                 |                                      |
| 30-30                                            | 2300                 | 71,000                | 23                       | 87.7                  | 5.09                    | 6.14                                 | 6.19                     | 6.67                                 | 3.9                                 | 2.5                                  |
| 40-0                                             | 2300                 | 50,500                | 17‡                      | 74.9                  |                         |                                      |                          |                                      | 2.9                                 |                                      |
| 40-40                                            | 2300                 | 82,500                | 29                       | 90.7                  | 5.49                    | 6.50                                 | 6.57                     | 7.05                                 | 3.0                                 | 2.0                                  |
| 50-0                                             | 2300                 | 63,500                | 23                       | 84.0                  |                         |                                      |                          |                                      | 2.9                                 |                                      |
| 50-50                                            | 2300                 | 89,500                | 39                       | 94.9                  | 5.75                    | 6.66                                 | 6.74                     | 7.23                                 | 3.0                                 | 1.7                                  |
| 40-40                                            | 2350                 | 84,500                | 27                       | 104.3                 | 5.40                    | 6.40                                 |                          |                                      | 3.6                                 | 2.2                                  |
| 50-50                                            | 2350                 | 92,000                | 38                       | 107.3                 | 5.76                    | 6.80                                 |                          |                                      | 4.3                                 | 1.2                                  |

\* Sintering time was 45 min at temperature.

† Shrinkage was measured on the 4 in. length of the tensile specimen.

‡ Specimen broke beyond gage marks.



Microstructural examination of these sintered stainless steel compacts reveals that at 2200°F and higher sintering temperatures ferrite is forming at grain boundaries. The amount of ferrite increases as the sintering temperature is raised as is shown in Figs. 3 and 4. This ferrite is the result of the high silicon content of the powder and the reduced carbon after sintering (the latter results from the decarburizing action of the hydrogen gas and of the small amount of oxide present). A small amount of ferrite is present for the short sintering treatment at 2200°F, Fig. 3, and with longer sintering times at higher temperatures this phase becomes almost continuous, Fig. 4. A few samples sintered at 2350°F show approximately 15 to 20 pct of ferrite as a continuous phase.

Because of the high strengths obtained on these powder compacts of stainless steel and the lack of data on a wrought material of similar analysis, a lot of stainless steel of the following composition was produced from a small ingot: C, 0.09 pct; Si, 2.65; Mn, 0.71; S, 0.006; P, 0.022; Cr, 17.74; and Ni, 8.32; density, 7.73 g per cc.

The tensile properties obtained are charted in Table VII. It is apparent that the high values of tensile strength obtained for these stainless steel

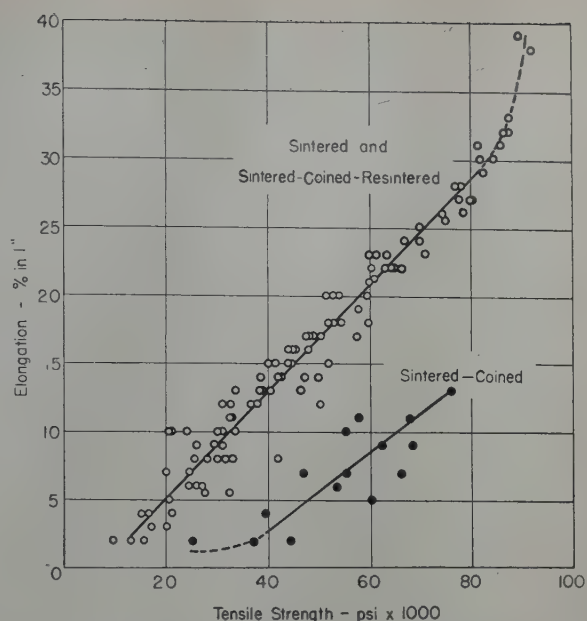


Fig. 2—Correlation of elongation and tensile strength for tensile specimens of all powders for all conditions. Solid circles, —100 mesh powder sintered at 2250°F in the as-coined condition.

Table VI. Properties of —100 Mesh Powder at 2250°F

| Compacting and Coining Pressure, Tons per sq in. | Sintering and Resintering Times, Min | Tensile Strength, Psi | Elongation, Pct in 1 in. | Hardness, Rockwell F | Green Density, g per cc | Density After First Sinter, g per cc | Coining Density, g per cc | Density After Final Sinter, g per cc | Shrinkage* During First Sinter, Pct | Shrinkage* During Second Sinter, Pct |
|--------------------------------------------------|--------------------------------------|-----------------------|--------------------------|----------------------|-------------------------|--------------------------------------|---------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| 30-0                                             | 15-0                                 | 16,500                | 4†                       | 36.8                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 30-30                                            | 15-0                                 | 25,000                | 2†                       | 81.5                 |                         |                                      |                           |                                      | 0.5                                 |                                      |
| 30-30                                            | 15-15                                | 32,500                | 11                       | 72.1                 | 5.10                    | 5.18                                 | 5.72                      | 5.76                                 | 0.7                                 | 0.4                                  |
| 40-0                                             | 15-0                                 | 24,500                | 7                        | 62.5                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 40-40                                            | 15-0                                 | 37,000                | 2                        | 91.8                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 40-40                                            | 15-15                                | 48,000                | 16                       | 67.7                 | 5.55                    | 5.61                                 | 6.18                      | 6.21                                 | 0.7                                 | 0.3                                  |
| 50-0                                             | 15-0                                 | 30,000                | 8                        | 70.9                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 50-50                                            | 15-0                                 | 44,500                | 2                        | 99.2                 |                         |                                      |                           |                                      | 0.6                                 |                                      |
| 50-50                                            | 15-15                                | 61,000                | 21                       | 86.1                 | 5.79                    | 5.87                                 | 6.46                      | 6.48                                 | 0.7                                 | 0.5                                  |
| 30-0                                             | 45-0                                 | 33,500                | 11                       | 67.6                 |                         |                                      |                           |                                      | 2.2                                 |                                      |
| 30-30                                            | 45-0                                 | 39,500                | 4†                       | 77.9                 |                         |                                      |                           |                                      | 2.1                                 |                                      |
| 30-30                                            | 45-45                                | 47,500                | 17†                      | 79.4                 | 5.16                    | 5.37                                 | 5.66                      | 5.90                                 | 1.8                                 | 1.2                                  |
| 40-0                                             | 45-0                                 | 40,000                | 15†                      | 69.6                 |                         |                                      |                           |                                      | 1.6                                 |                                      |
| 40-40                                            | 45-0                                 | 53,500                | 6                        | 92.1                 |                         |                                      |                           |                                      | 1.9                                 |                                      |
| 40-40                                            | 45-45                                | 65,000                | 22                       | 87.1                 | 5.55                    | 5.72                                 | 6.15                      | 6.28                                 | 1.6                                 | 1.4                                  |
| 50-0                                             | 45-0                                 | 47,500                | 14†                      | 75.7                 |                         |                                      |                           |                                      | 1.6                                 |                                      |
| 50-50                                            | 45-0                                 | 60,500                | 5                        | 99.2                 |                         |                                      |                           |                                      | 1.6                                 |                                      |
| 50-50                                            | 45-45                                | 77,000                | 28                       | 92.5                 | 5.85                    | 6.00                                 | 6.46                      | 6.61                                 | 1.5                                 | 1.3                                  |
| 30-0                                             | 90-0                                 | 38,500                | 13                       | 68.5                 |                         |                                      |                           |                                      | 3.2                                 |                                      |
| 30-30                                            | 90-0                                 | 47,000                | 7                        | 83.9                 |                         |                                      |                           |                                      | 3.2                                 |                                      |
| 30-30                                            | 90-90                                | 58,000                | 19†                      | 80.8                 | 5.10                    | 5.49                                 | 5.73                      | 6.03                                 | 3.1                                 | 1.4                                  |
| 40-0                                             | 90-0                                 | 51,500                | 20                       | 74.6                 |                         |                                      |                           |                                      | 2.8                                 |                                      |
| 40-40                                            | 90-0                                 | 55,500                | 7                        | 92.6                 |                         |                                      |                           |                                      | 2.3                                 |                                      |
| 40-40                                            | 90-90                                | 66,500                | 22†                      | 88.9                 | 5.54                    | 5.90                                 | 6.17                      | 6.47                                 | 2.3                                 | 1.3                                  |
| 50-0                                             | 90-0                                 | 57,500                | 17                       | 87.8                 |                         |                                      |                           |                                      | 2.8                                 |                                      |
| 50-50                                            | 90-0                                 | 68,500                | 9                        | 98.0                 |                         |                                      |                           |                                      | 2.8                                 |                                      |
| 50-50                                            | 90-90                                | 82,000                | 30                       | 94.4                 | 5.77                    | 6.12                                 | 6.43                      | 6.71                                 | 2.5                                 | 1.1                                  |
| 30-0                                             | 180-0                                | 45,000                | 16                       | 69.2                 |                         |                                      |                           |                                      | 3.9                                 |                                      |
| 30-30                                            | 180-0                                | 55,500                | 10                       | 86.9                 |                         |                                      |                           |                                      | 3.9                                 |                                      |
| 30-30                                            | 180-180                              | 60,000                | 23                       | 81.5                 | 5.09                    | 5.77                                 | 5.90                      | 6.22                                 | 3.0                                 | 1.1                                  |
| 40-0                                             | 180-0                                | 53,000                | 20                       | 81.8                 |                         |                                      |                           |                                      | 2.7                                 |                                      |
| 40-40                                            | 180-0                                | 62,500                | 9                        | 95.9                 |                         |                                      |                           |                                      | 3.0                                 |                                      |
| 40-40                                            | 180-180                              | 75,000                | 28                       | 84.9                 | 5.48                    | 6.14                                 | 6.31                      | 6.65                                 | 3.0                                 | 1.2                                  |
| 50-0                                             | 180-0                                | 54,500                | 18†                      | 71.9                 |                         |                                      |                           |                                      | 2.4                                 |                                      |
| 50-50                                            | 180-0                                | 66,500                | 7†                       | 100.8                |                         |                                      |                           |                                      | 2.3                                 |                                      |
| 50-50                                            | 180-180                              | 87,500                | 33                       | 95.3                 | 5.80                    | 6.35                                 | 6.55                      | 6.81                                 | 2.6                                 | 1.2                                  |
| 30-0                                             | 300-0                                | 48,500                | 17†                      | 74.8                 |                         |                                      |                           |                                      | 3.9                                 |                                      |
| 30-30                                            | 300-0                                | 58,000                | 11                       | 81.4                 |                         |                                      |                           |                                      | 4.1                                 |                                      |
| 30-30                                            | 300-300                              | 67,000                | 24                       | 79.9                 | 5.22                    | 6.01                                 | 6.09                      | 6.34                                 | 4.1                                 | 1.2                                  |
| 40-0                                             | 300-0                                | 61,500                | 23                       | 83.7                 |                         |                                      |                           |                                      | 3.8                                 |                                      |
| 40-40                                            | 300-0                                | 68,000                | 11                       | 98.1                 |                         |                                      |                           |                                      | 3.6                                 |                                      |
| 40-40                                            | 300-300                              | 81,500                | 31                       | 94.0                 | 5.57                    | 6.51                                 | 6.55                      | 6.85                                 | 3.2                                 | 1.5                                  |
| 50-0                                             | 300-0                                | 64,500                | 22†                      | 85.5                 |                         |                                      |                           |                                      | 3.0                                 |                                      |
| 50-50                                            | 300-0                                | 76,500                | 13                       | 99.7                 |                         |                                      |                           |                                      | 3.1                                 |                                      |
| 50-50                                            | 300-300                              | 87,500                | 32†                      | 97.1                 | 5.87                    | 6.69                                 | 6.81                      | 7.06                                 | 3.0                                 | 1.2                                  |

\*Shrinkage was measured on the 4 in. length of the tensile specimen.

† Specimen broke beyond gage marks.



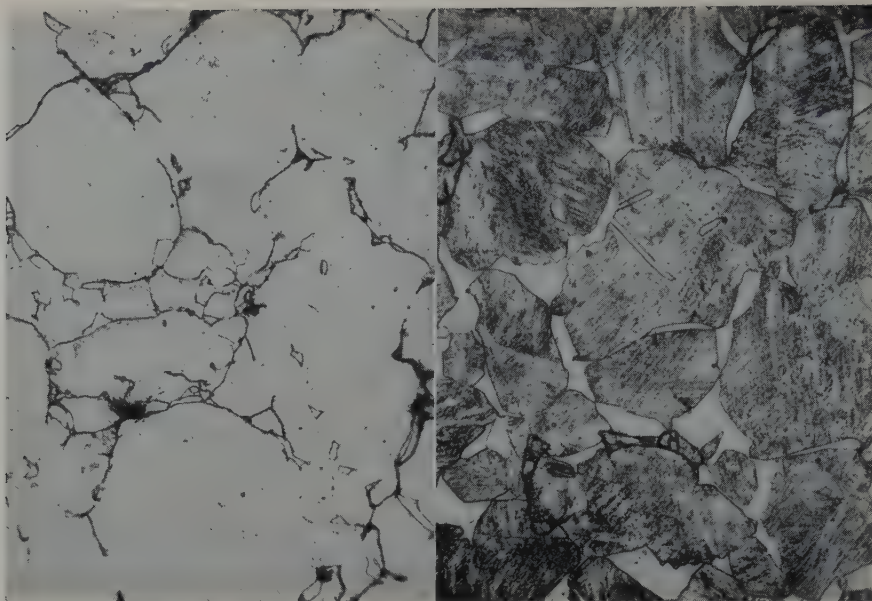


Fig. 3 (left)—Structure of tensile specimen prepared from —100 mesh powder pressed at 30 tons per sq in. and sintered 45 min at 2200°F. Etchant, Marble's reagent. X500. Reduced approximately 50 pct for reproduction.

Fig. 4 (right)—Structure of tensile specimen prepared from —100 mesh powder pressed at 50 tons per sq in. Sintered 45 min at 2300°F. Coined at 50 tons per sq in. and resintered 45 min at 2300°F. Etchant, Marble's reagent. Samples taken near tensile fracture showing effect of deformation on matrix structure. X500. Reduced approximately 50 pct for reproduction.

powder compacts by normal powder metallurgy techniques approach those of the wrought material. Ductility is, as expected, relatively lower and could only be increased by increasing the density through extra cold coining and sintering or hot coining operations.

The tensile samples of wrought material had visible amounts of ferrite only at the surfaces which were decarburized during the hydrogen treatment. This is probably responsible for the slight drop in tensile strength as the treating temperature was raised and confirms the supposition that the ferrite in the compacts from the stainless steel powder is partly the result of decarburization throughout the slightly porous compact.

The carbon content of the compacts decreased to at least 0.05 pct at 2100°F and to 0.00 to 0.02 pct at 2300°F. This loss of carbon is accompanied by a weight loss due to the reduction of oxides which under even the most severe conditions of sintering times and temperatures did not exceed 0.35 pct.

### Conclusions

1. A prealloyed 18-8 stainless steel powder has been developed that is readily moldable, can be sintered at temperatures as low as 2100°F in a hydrogen atmosphere, and yields compacts with higher strengths and ductility than heretofore possible by standard powder metallurgy techniques.

2. The powder containing 2.50 pct Si is free flowing with an apparent density of 2.9 g per cc and a maximum weight loss in hydrogen of 0.35 pct.

3. Optimum pressing and sintering conditions vary with the screen analysis, the finer powders being capable of handling at slightly lower pressures and temperatures. For —100 mesh standard powder pressing at 40 tons per sq in. and sintering for 45 min at 2250°F gives a tensile strength of 40,000 psi and an elongation of 15 pct. Coining at 40 tons and resintering at 2250°F for 45 min provides a tensile strength of 65,000 psi and an elongation of 22 pct.

4. The highest properties realized for the —100 mesh powder were 87,000 psi tensile strength with 32 pct elongation. For a special blend of fine powder these values were 92,000 psi and 38 pct, respectively. These strength properties approach those for wrought material of the same composition.

5. Tensile strength and elongation show a straight-line relationship for this powder, regardless of screen analysis or pressing and sintering conditions. Coining, not followed by resintering, however, lowers elongation while raising tensile strength.

6. Silicon promotes the formation of small quantities of ferrite at high sintering temperatures, especially as the hydrogen atmosphere reduces the carbon content of the compacts to below 0.02 pct.

### Acknowledgment

The assistance of Lester M. Gibson in the work of specimen preparation and testing is gratefully acknowledged.

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Table VII. Tensile Properties Obtained

| Treatment*        | Tensile Strength, psi | Elongation in 1 in., Pct |
|-------------------|-----------------------|--------------------------|
| 45 min at 2100°F  | 105,000               | 74                       |
| 45 min at 2200°F  | 102,000               | 72                       |
| 45 min at 2250°F  | 99,000                | 72                       |
| 45 min at 2300°F  | 99,500                | 68                       |
| 15 min at 2100°F* | 108,500               | 74                       |

\* All samples cooled in water cooled zone of tube furnace as per powder samples except starred item which was water quenched.



# Preparation of Titanium Tetrachloride from Rutile

by C. H. Gorski

A method for preparing titanium tetrachloride is described which consists of reducing rutile with coke and chlorinating the reduced product at 200° to 500°C. The crude distillate is purified by treatment with copper powder and distillation. Recoveries, exceeding 90 pct of the titanium in the rutile, were obtained.

IN recent years considerable interest in metallic titanium has been aroused because of its outstanding physical and chemical properties. The present commercial processes for preparing titanium are modifications of the Kroll<sup>1</sup> process and consist essentially of the reduction of titanium tetrachloride with magnesium in an inert atmosphere to produce metallic titanium with magnesium chloride as a byproduct.

At present,<sup>2</sup> commercial titanium tetrachloride costs \$0.32 a pound, which makes the price of the included titanium \$1.28 a pound. As the titanium tetrachloride must be purified further before processing into metal, its ultimate cost obviously will be higher. Consequently, one of the prime requisites for the production of lower cost titanium metal is a source of low-cost titanium tetrachloride.

Recently, Knickerbocker, Gorski, Kenworthy, and Starliper<sup>3</sup> described a method for preparing titanium tetrachloride from low-grade Arkansas rutile by smelting the rutile with pyrite and coke to form a titanium matte and then chlorinating the titanium matte to prepare a crude titanium tetrachloride. This process had several inherent advantages. Low-grade rutile concentrates were utilized, the chlorination temperature was relatively low (approximately 200°C), and the reaction was strongly exothermic. However, this process had several disadvantages, chief of them being the rather low recoveries of titanium tetrachloride (65 to 81 pct) and the difficulty in purifying the crude titanium tetrachloride obtained.

Because of the high-titanium and low-iron con-

tents of rutile as compared to ilmenite, rutile should be of greater potential value as a source of titanium tetrachloride than ilmenite. Rutile, however, is not chlorinated directly in commercial practice, because reaction temperatures above 700°C are required, at which point chlorine attacks most of the common materials of construction. The process now in use consists of converting the titanium in rutile to the cyanonitride by high-temperature reduction in an electric furnace, and then chlorinating this compound. The disadvantages of this process are the difficulty of producing the cyanonitride, the use of high-grade rutile concentrates in the charge, and the presence of several percent of silicon tetrachloride in the finished product. It would be of considerable interest to develop a new process for the preparation of titanium tetrachloride from rutile by chlorination at 200° to 500°C.

## Process Development

Several investigators<sup>4-7</sup> have studied the reduction of titanium dioxide with carbon in an effort to prepare titanium monoxide. Invariably, the titanium monoxide formed in this manner was not pure, as it contained titanium carbide and one or more of the lower oxides of titanium. As these lower oxides of titanium are more reactive chemically than rutile, and as it is known that titanium carbide may be chlorinated readily, a study was made of the chlorination of carbon-reduced rutile. A sample of rutile concentrates from Hot Spring County, Ark., containing 76.19 pct TiO<sub>2</sub>, 5.65 pct Fe<sub>2</sub>O<sub>3</sub>, 4.18 pct SiO<sub>2</sub>, and 2.88 pct Al<sub>2</sub>O<sub>3</sub>, was used for this investigation.

The experimental procedure consisted of making an intimate mixture of —100-mesh rutile and petroleum coke, adding water and molasses as a binder to form a paste, charging into a graphite crucible that was covered, except for a vent to allow the

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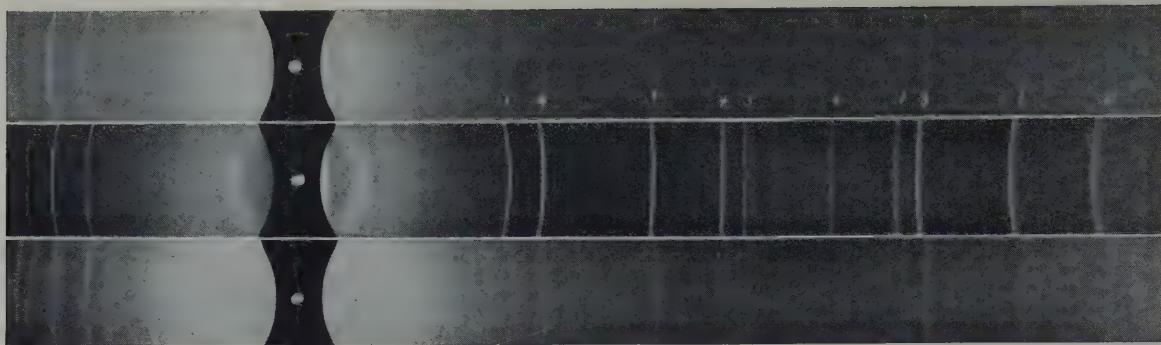


Fig. 1 (top)—Rutile reduced at 1400°C with coke.

Fig. 2 (center)—Titanium carbide.

Fig. 3 (bottom)—Rutile reduced at 1200°C with coke.

escape of gases, and heating with a 3.0 kva high-frequency induction furnace. The charge was held at the reaction temperature (1050° to 1400°C) for 30 min and permitted to cool in the absence of air. After cooling, the charge, which was in the form of a sinter, was ground to —100-mesh, mixed with 30 pct of its weight of —100-mesh petroleum coke, and chlorinated. (The petroleum coke had the following chemical analysis: 79.0 pct fixed carbon, 13.8 pct volatile combustible matter, 6.5 pct ash, and 0.72 pct moisture.) Chlorination was effected in a quartz tube heated by a tube furnace held in a vertical position. The chlorine flowed up through the charge, and the reaction product, which consisted essentially of titanium tetrachloride with minor amounts of ferric chloride, was passed through the top end of the quartz tube, condensed in an air condenser, and collected in a 500-ml wide-mouthed Erlenmeyer flask. The exit gas was bubbled through a flask containing concentrated hydrochloric acid to keep air from entering the system in case the chlorine flow was halted temporarily. The crude titanium tetrachloride was purified by one of several methods described later.

#### Effect of Experimental Variables

Several series of runs were made to study the effect of varying the amount of petroleum coke and reaction temperature on the reduction of rutile and subsequent chlorination of the reduced product.

In the first series of experiments, each charge consisted of 250 g of rutile concentrates, 37 g of petroleum coke, 14 g of molasses, and 33 g of water. Sufficient coke was used so that its fixed carbon content was approximately equal to the stoichiometric amount of carbon necessary to reduce the titanium dioxide content of the rutile concentrates to titanium monoxide. The samples were heated for 30 min at 1100° to 1400°C. The chemical analyses of these reduced products are shown in Table I. The amounts of titanium and combined carbon in the samples decreased as the reduction temperature was lowered.

Chlorination of the reaction products at 500°C showed titanium recoveries of 98 pct or more could be obtained from the samples furnace at 1300° and 1400°C. The samples furnace at 1100° to 1200°C gave titanium recoveries of approximately 90 pct.

In another series of experiments the temperature was held constant at 1400°C, the amount of rutile was 250 g, the amount of petroleum coke used was increased from 37 g in stages to 66.6 g, and the

molasses was similarly increased from 14.0 to 15.8 g. Chlorination of these samples at 500°C gave titanium recoveries of 95 to 99 pct. Increasing the amount of coke in the induction furnace charges had no marked effect upon the recovery of titanium by chlorination at 500°C. When the amount of coke was increased, however, it was possible to lower the chlorination temperature to as low as 200°C and recover more than 90 pct of the titanium.

An overall summary of several runs, showing the chemical analyses of the chlorination residues, the chlorination conditions, the conditions under which the rutile was reduced, and the titanium recoveries obtained, is shown in Table II. In these runs each sample was chlorinated until there was no further reaction, as indicated by the absence of vapor passing through the condenser.

More than 95 pct titanium could be recovered consistently when rutile was reduced at 1200° to 1400°C with an excess of petroleum coke and then chlorinated at 500°C. When the reduction temperature was less than 1050°C, the titanium recovery was lowered considerably.

Further experimental work showed that the reduced rutile could be chlorinated at temperatures as low as 136° to 144°C, approximately the normal boiling point of titanium tetrachloride, with a recovery of 84.6 pct of the titanium in the rutile.

#### Purification of Titanium Tetrachloride

The product obtained by the chlorination of reduced rutile consisted primarily of titanium tetrachloride and ferric chloride with minor amounts of sulphur chloride and other unidentified compounds. Simple distillation of this crude product gave a titanium tetrachloride containing 0.27 pct iron and 0.09 pct sulphur. This product obviously is not pure enough for use in preparing titanium metal.

Several schemes of purification were tried in an

Table 1. Chemical Analyses of Reduced Rutiles

| Run No. | Reduction Temp, °C | Analysis, Pct |     |           |          |
|---------|--------------------|---------------|-----|-----------|----------|
|         |                    | Ti            | Fe  | C (comb.) | C (free) |
| 1       | 1,400              | 52.0          | 5.8 | 2.8       | 2.2      |
| 2       | 1,300              | 51.5          | 4.5 | 2.4       | 1.4      |
| 3       | 1,200              | 49.8          | 4.4 | 2.1       | 3.8      |
| 4       | 1,100              | 48.7          | 4.7 | 1.7       | 4.2      |



effort to prepare titanium tetrachloride at least as pure as titanium tetrachloride currently sold as a reagent of cp grade. These consisted of treatment of single-distilled titanium tetrachloride with hydrogen sulphide followed by distillation, treatment of single-distilled titanium tetrachloride with calcium hydride<sup>8</sup> followed by distillation, direct treatment of crude titanium tetrachloride with copper powder followed by distillation, and treatment of single-distilled titanium tetrachloride with copper powder followed by distillation.

The most effective method of purification consisted of agitating the single-distilled titanium tetrachloride with 2 pct of its weight of copper powder for 1 hr at 100°C and again distilling. A water-white distillate was obtained that was spectrographically equal to or better than cp titanium tetrachloride in every respect. The titanium recovery in this step should be 95 pct or better.

Hydrogen sulphide gave promising results as a purification agent. Further research probably would show it to be as effective as the copper-powder treatment. Calcium hydride was ineffective as a purification agent. The titanium tetrachloride prepared by the hydride addition was considerably higher in vanadium than cp titanium tetrachloride.

The method of analyzing titanium tetrachloride has been outlined by Stoddard and Pietz<sup>9</sup> and consisted of hydrolyzing the titanium tetrachloride and running a spectrographic analysis of the product of hydrolysis. A sample of titanium tetrachloride, currently sold as a reagent of cp grade, was run in the same manner and was compared with each of the titanium tetrachloride samples prepared in the laboratory.

A chemical analysis of cp titanium tetrachloride showed 0.006 pct iron and 0.008 pct silicon. The pure titanium tetrachloride made by treatment with copper followed by distillation was water-white and by spectrographic analysis contained equal or smaller amounts of impurities than the commercial cp product. The cp titanium tetrachloride was straw-colored. This discoloration was caused partly by the presence of vanadium compounds and partly by chlorine dissolved in the liquid.

### X-Ray Analysis

Several X-ray diffraction patterns were made of some of the samples of reduced rutile in an effort to identify the major constituents. The data were

obtained with a 143.2 mm diam Debye-Sherrer camera. The sample was mounted on a fine-drawn pyrex fiber with collodion and rotated in an X-ray beam passing through a 0.030-in. diam collimator for a 3-hr exposure.

The X-ray diffraction patterns for titanium carbide and titanium monoxide are very similar, and it was impossible to differentiate between these compounds by X-ray analysis. The samples reduced at 1300° to 1400°C were essentially mixtures of titanium carbide and titanium monoxide, whereas those reduced at 1100° to 1200°C contained minor amounts of titanium suboxide ( $Ti_2O_3$ ) in addition to titanium carbide and monoxide. Diffraction patterns of rutile and of titanium carbide are shown in Figs. 1 to 3.

### Summary

A relatively simple method of preparing titanium tetrachloride has been developed. This process consists in reducing the rutile with coke at 1100° to 1400°C to form a reduction product identified as a mixture of titanium suboxides and minor amounts of titanium carbide. This reduced product is then chlorinated at 200° to 500°C to form a crude titanium tetrachloride, which may be purified by distillation and treating the singly distilled product with copper powder and redistilling. The product thus obtained was equal to or greater in purity than titanium tetrachloride currently sold as a reagent of cp purity. In this manner 90 pct or more of the titanium in the rutile has been recovered.

The chief advantage of this method of preparing titanium tetrachloride is the low chlorination temperatures (200° to 500°C). The product is substantially free from silicon compounds, thus making the purification simpler than the purification of commercial, technical grade titanium tetrachloride, which usually contains several percent of silicon tetrachloride.

### Acknowledgments

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Table II. Overall Summary of Chlorination Runs

| Run No. | Reduction Conditions                | Chlorination Conditions  | Residue Analysis, Pct |     |         | Titanium Chloride Recovery, Pct |
|---------|-------------------------------------|--------------------------|-----------------------|-----|---------|---------------------------------|
|         |                                     |                          | Ti                    | Fe  | Total C |                                 |
| 10      | 1300°C with 13 pct excess of coke*  | 7 hr at 500°C            | 2.0                   | 0.9 | 59.1    | 98.3                            |
| 11      | 1200°C with 75 pct excess of coke   | 5 hr and 20 min at 200°C | 8.1                   |     | 48.8    | 91.1                            |
| 12      | 1400°C with 11.2 pct excess of coke | 5 hr at 500°C            | 1.6                   | 2.8 | 38.7    | 98.2                            |
| 13      | 1000°C with 13 pct excess of coke   | 3 hr at 500°C            | 15.2                  |     | 43.2    | 79.0                            |
| 14      | 1200°C with 13 pct excess of coke   | 7 hr and 20 min at 500°C | 4.0                   | 1.7 | 49.5    | 96.3                            |

\* Excess of coke means the excess above that necessary to reduce the titanium dioxide content of the rutile to titanium monoxide. In these calculations it was assumed that only the fixed carbon content of the coke took part in the reaction.



# Reverse Leaching of Zinc Calcine

by L. P. Davidson, R. K. Carpenter, and H. J. Tschirner

THE electrolytic zinc plant of the American Zinc Co. of Illinois, at Monsanto, was expanded in 1943 to a capacity of 100 tons of slab zinc daily. This capacity was not attained because of inability of the leaching plant to deliver an adequate amount of solution for electrolysis. Changing the leaching method so that the acid was added to the roasted zinc material reversed the usual procedure and made it possible to attain the desired capacity. The conditions which prevented satisfactory work before this change and the difficulties which arose in reversing the usual leaching procedure are described.

The "reverse" leach operation as now practiced is carried out as follows: All the calcine to be leached is fed continuously to a slurry mixing tank. About one third of the acid to be used is fed to the tank with the calcine. The slurry is discharged continuously to a Dorr duplex classifier in closed circuit with a Hardinge mill. The classifier overflow is pumped to any of six leaching tanks where the leach is completed.

A finished leach is discharged through Allen-Sherman-Hoff pumps to Dorr thickeners, from which the overflow goes to the zinc dust purification and the underflow to vacuum filters.

This change in leaching procedure from the usual one of adding calcine to a large amount of acid made it possible to provide an adequate amount of purified solution to the electrolyzing division and at the same time filter and dry all the residue produced. Operating savings in reagents and better metallurgical recoveries were also important benefits.

The original flowsheet of the leaching plant provided leaching, sedimentation of the insoluble residue, and purification of the neutral zinc sulphate solution with zinc dust. The thickened residue was filtered and washed. The purification cake of excess zinc dust, precipitated copper and cadmium, and any insoluble residue was filtered off on plate-and-frame duplex classifier.

Settlement in the thickeners was inadequate and the suspended solids in the thickener overflow gave rise to filtration difficulties after the zinc dust purification. Further, the filtration and washing of the leach residue was poor, and it became necessary to pump a large amount of unwashed or poorly washed residue to storage ponds outside the plant building.

Two causes of the poor settling and filtration were determined: Soluble silica and ferrous iron in the calcine treated. The latter was a result of poor roasting and with more experience ceased to be a major

problem. The silica was a normal constituent of the feed and the working out of the problem became a matter of controlling its solubility.

The obvious method to render the silica insoluble was by intensive roasting. This, however, met with total failure as such roasting resulted in silicates, probably zinc, soluble in the 13 pct acid used for leaching. Attempts were made to coagulate the fine gelatinous slime with addition agents. Glue, lime, starch, beef-blood serum and others were tried without success. All the suggested tried-and-tested means of operating the thickeners gave no consistently good results. Variations in leaching time, in addition of calcine to the leaching tanks, "conditioning" of the pulp by prolonged agitation, immediate discharge of the leach upon completion to avoid breaking up flocs were all tried and given up as ineffective.

Byron Marquis, of Singmaster and Breyer, worked with the plant staff on a beaker scale until a leaching procedure was developed which gave consistent results and a promise of overcoming the difficulties which had plagued the plant operation. It was suggested that the difference in solubility of silicates and zinc oxide in sulphuric acid could be made use of in a leaching method where the acidity was controlled carefully. Such control is possible when acid is added to a slurry of calcine. This process reverses the normal procedure of adding calcine to a vessel of acid, hence the term "reverse leach" was applied.

In this way, the overall acid concentration can be kept very low. In the tests made, it did not exceed 0.05 g per liter free sulphuric acid.

Numerous advantages were realized when no silicates were taken into solution and later precipitated as a bulky gel. The gel had made reasonable thickening and filtration of the leach pulp and practical drying of the residue impossible. When the gel was eliminated, thickening rates were increased as much as five times. The volume of residue after thickening represented about 10 pct of the total leach pulp and had been as high as 95 pct when the gel was present. The thickened pulp was filterable and the filtered cake was dried readily after washing.

The zinc extraction from the calcine was slightly lower. This was more than compensated for by the increase in zinc recovered in solution from zinc which had been trapped in the gelatinous residue. The amount of copper recovered was lower. However, the amounts of other impurities, such as arsenic, antimony, and germanium, taken into solution were lower. This was particularly true of antimony. Since the inception of reverse leaching, no concentrates have failed to yield solutions free of antimony even when present in the calcine to the extent of 0.2 to 0.3 pct.

Oxidation of ferrous iron is a problem of reverse leaching. Ferrous hydrate does not precipitate at pH 5.3 to 5.4 where a leach is finished. The usual oxida-

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tion to the ferric state with manganese dioxide is not possible because of the low concentration or absence of free sulphuric acid. An excess of calcine will precipitate the ferrous iron but this method wastes calcine, results in a very viscous pulp which tends to cake in pumps and pipe lines, and places an undue load on the thickener mechanisms. Soluble copper will catalyze the oxidation of ferrous iron to the ferric state when air is passed through the pulp. A low-pressure air line was introduced into each leaching tank and the soluble copper normally present in the solution was sufficient for oxidation.

The question arose as to the solution of zinc oxide in sulphuric acid at concentrations of 0.05 g per liter. Tests showed that when stoichiometric quantities of zinc oxide and 200 g per liter sulphuric acid were reverse leached, 98 pct of the zinc oxide was dissolved. After 15 min the pH was 2.5. An additional 2 pct zinc oxide raised the pH to 5.8, the maximum which could be attained, even with 100 pct excess.

After the leaching technique had been developed, complete cyclic electrolyzing tests were made with solutions from various calcines. When these results proved satisfactory, pilot-plant work was started to determine equipment for this process on plant scale.

A slurry of zinc oxide and zinc sulphate solution will cement and "set up." This slurry could not be made in the leaching tanks because of this tendency and because zinc extraction from the large cemented lumps is low. The preparation of the slurry, of necessity, had to be carried out in equipment outside the leach tanks. Standard classifying, grinding and pumping equipment was found to be adequate. Many trials were made before a satisfactory mixing vessel was developed.

### Development of Equipment

The reverse leach flowsheet, as illustrated in Fig. 1, was installed in the plant in the summer of 1944. A Merrick Feed-O-Weight was chosen to weigh and feed the calcine to the mixing equipment. With this, the collection and feeding of the calcine from the 12 storage bins became automatic. A 6-in. horizontal screw feeder was provided in the pyramidal bottom of each bin. The screw is totally encased except that portion in the bin which operates in a semicircular trough. Each is motor driven through a Reeves variable speed control. Two 10-in. collection screws, each conveying the calcine from six bin feeders, discharge into the scale hopper of the Feed-O-Weight. Operation of the conveyors is intermittent and controlled by Bindicators on the scale hopper. This system permits the selection and blending of calcines to make up a uniform plant feed since the rate of withdrawal from any bin can be controlled.

The blended calcine was fed into the slurry mixer along with purified solution assaying 135 g per liter zinc. It was imperative to agitate this pulp continuously and guard against temperatures over 45°C, because such a slurry on standing or heating quickly formed a zinc oxy-sulphate cement.

The slurry mixer was a three volume-ton, top discharge tank provided with a 22 in. duplex turbo mixer driven by a 5 hp motor geared to 350 rpm. The impeller was 6 in. from the tank bottom. The overflowing slurry was laundered to a standard Dorr duplex classifier.

The oversize material from the classifier was ground in a 4½ ft x 16 in. conical Hardinge ball mill in closed circuit with the classifier. Classifier overflow was piped to a 125 gpm Allen-Sherman-Hoff

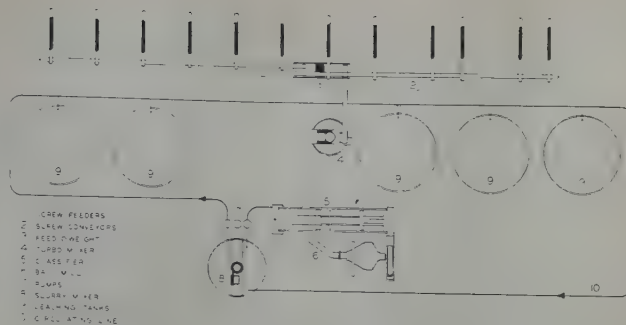


Fig. 1—Reverse leach flowsheet.

Packless rubber-lined pump and pumped through a 4-in. line to a 25 volume-ton Dorr slurry mixer used as a surge tank. A 4-in. circulating line was provided between the surge and leaching tanks.

The slurry was leached in 40 volume-ton, cone bottom, mechanically agitated tanks. These tanks, 14 ft deep x 10 ft in diam, are constructed of lead-lined steel with a 4-in. acid-proof brick inner-lining. A 1-in. copper line introduces compressed air beneath the center of the agitator shaft. These tanks discharge into a 5-in. copper manifold leading to two 500 gpm Allen-Sherman-Hoff Packless pumps, discharging in turn into three 50-ft Dorr thickeners in parallel.

The thickener overflow was laundered to the zinc dust purification tanks. The underflow was filtered and washed on Moore filters. The residue then was repulped with water and refiltered on three Eimco filters. The dewatered cake was dried in a rotary drier and shipped.

Within 24 hr of operation, all the slurry piping, except vertical sections, cemented shut. The cementing occurred first in valves, tees, and short nipples and progressed from there. The air agitating outlets in the surge tank cemented shut. This was the first difficulty encountered.

The surge tank was discarded. The circulating line was replaced by open wooden launders. The slurry pump was coupled as closely as possible to the overflow from the classifier with a 4-in. flanged rubber coupling. A vertical 4-in. copper line was installed to conduct slurry from the pump to the highest point in the launder distributing system.

In mixing the calcine and zinc sulphate solution more difficulties arose. A crust of cemented slurry soon formed at the top of the turbo-mixer. This cementation was not eliminated by relocating or providing an additional impeller. The mixer was replaced by a mixing launder in which neutral zinc sulphate solution entered through a perforated bottom and was met by the calcine from the top. Subsequently, calcine was dropped into an inclined launder onto a stream of solution. The operation was fairly satisfactory but extremely dusty. Frequent cleaning of the pipe and launders was necessary.

This method was used in the plant until it was found that the slurry could be made satisfactorily by mixing an excess of calcine with spent electrolyte. Replacing the zinc sulphate solution with spent electrolyte made possible the use of a large, vented, bottom-discharge mixing tank, which discharged the slurry continuously through an air lift into the classifier. Mild steel plate and rakes were satisfactory in the classifier with the zinc sulphate-calcine slurry. The use of spent electrolyte introduced soluble copper and resulted in severe corrosion. Stain-

less steel rakes were installed first and eventually all exposed parts of the classifier and other equipment were replaced with stainless steel.

Early in 1950, the launder system was replaced by a stainless steel distribution box with rubber hose lines from the box to the individual leaching tanks.

Now the slurry is made in a stainless steel tank where the calcine is mixed with the acid and discharged through the air lift to the classifier. The feeding of the calcine, spent electrolyte, and iron solution is controlled and proportioned automatically. Adequate suction is provided by a small fume scrubber so that the operation is dust and vapor free. About one third of the leaching takes place in this tank. The cementing problem is minimized by the increase in the solution: solid ratio and the reduction in the amount of free zinc oxide present for cement formation.

Thickener underflow was filtered originally on Moore filters. It was found that these filters were unsatisfactory for the new pulp, because the consistency was such that heavier particles settled out in the filter tanks. This had not been the case when the voluminous silica gel was present. Air agitation was not successful in keeping heavier particles in suspension. The cake picked up on the Moore filter dewatered so fast that it was impossible to transfer it to the wash tank before the cake cracked badly. Further, once cracked, portions of the heavy cake, especially around the bottom of the leaves, fell off. Both of these conditions made satisfactory washing impossible.

Therefore, the thickened pulp was pumped directly to the Eimco filters. Filtration was satisfactory but washing was not. A cake in excess of  $\frac{1}{2}$  in. was necessary for proper discharge. The water-soluble zinc in such a cake was not removed during the washing time available. Residues high in water-soluble zinc were difficult to dry.

An unforeseen condition of the thickened reverse-leach pulp led to a change in the thickener operation. When this pulp has aged more than 48 hr, it becomes extremely viscous and difficult to filter, and there is a retention of zinc sulphate. The filtrate from an aged pulp will contain less zinc than the solution in which it has thickened. The difference is as much as 60 g per liter zinc. It can be recovered by washing the filter cake with water. The first displacement and as high as the first three displacements of liquor in the filter cake, depending on the time the pulp has aged, will contain more zinc than the original filtrate. An aged pulp requires a large amount of water and much time to wash the filter cake free of zinc sulphate, or in other words, more filter capacity for the same amount of solids.

In making the changes outlined to overcome the difficulties encountered, a very satisfactory and workable process has been developed.

### Operations

Calcine, as-received, is fed at a uniform rate from the storage bins into the mixing tank. Return electrolyte is added to maintain a slurry density of about 1.5 sp gr. This density permits classification at 100 mesh. Oversize material is ground in the ball mill and returned to the classifier. A typical screen analysis of the ground slurry is given in Table I. Grinding to smaller particle size does not increase the zinc extraction materially.

Slurry containing 4.5 to 5 tons of equivalent calcine is fed to one of six leaching tanks which will

Table I. Screen Analysis of Ground Slurry

| Mesh | Pct |
|------|-----|
| 35   | Nil |
| 65   | 1   |
| 100  | 3   |
| 150  | 6   |
| 200  | 10  |
| -200 | 80  |

contain a "heel" of return electrolyte just covering the agitator. This is neutralized so rapidly that little or no silica is taken into solution. Slurry addition is timed, 30 min per tank, since the weighing device is set to deliver the calcine for one leach in that time.

Acid containing from 0.5 to 1.0 g per liter iron as ferric sulphate is added to the slurry until a test of the pulp at the top of the tank shows acid to methyl-orange indicator. The acid addition is stopped until the test shows neutral or basic to methyl-orange. Then, more acid is added until a positive test again occurs. This is repeated until the acidity persists for about 3 min, which is the point of maximum zinc extraction, and the leach would be complete except for the presence of ferric sulphate. Precipitation of ferric hydroxide occurs here with the release of some free sulphuric acid which must be neutralized. A small amount of slurry is added. Completeness of iron precipitation is checked with ammonium thiocyanate test papers. Small amounts of ferrous iron are oxidized by compressed air introduced beneath the agitators and dispersed through the leach. The copper required for this reaction originates from the calcine. Ferrous iron occurs only in those calcines which have not been roasted thoroughly.

While satisfactory washing could be attained using a cotton twill filter cover, blinding of the cloth and decreasing filtration rate with time required frequent changes of the cover. In 1948, a nylon filter cover was used for the first time with excellent results. This is a specially woven cloth with tightly twisted yarn in which filtering is only through the fabric openings. The only blinding comes from precipitation of gypsum and this has been largely overcome by the use of low-pressure steam instead of air for the blow-off.

Summed up, the operating difficulties which called for correction because of inability to attain the rated capacity of the plant were:

1. Difficult and slow filtration of the purified solution.
2. Absence of clear overflow from the thickener.
3. Inability to filter and wash residue.
4. Inability to dry residue.
5. Wasteful impounding of residue.
6. Wasteful consumption of sulphuric acid, manganese dioxide, and calcine.

The introduction of "reverse" leaching has made it possible to:

1. Provide an adequate amount of purified solution.
2. Have 8 to 10 ft of clear solution in the secondary thickeners.
3. Filter and wash effectively the entire residue output.
4. Dry all the residue filtered.
5. Stop the impounding of unwashed residue.
6. Cut the consumption of sulphuric acid, manganese dioxide, and calcine.



# Metallurgical Reactions of Fluorides

by Herbert H. Kellogg

Graphs representing the standard free-energy of formation as a function of temperature for 21 fluorides are presented, along with estimated values for the standard free-energy of formation of 20 additional fluorides. A few of the many possible uses of these data in metallurgical calculations are discussed, including the fluorination of oxides, sulphides, and chlorides, and the reduction of metal fluorides.

RECENT papers which have presented free-energy data for oxides, sulphides, chlorides, carbonates, sulphates, and silicates in the form of free energy vs. temperature plots,<sup>1-5</sup> have found important uses in teaching and metallurgical development work. This method of presentation of thermodynamic data serves to make available in readily usable form thermodynamic constants which are scattered throughout the literature, and to show by graphical means the stability relations which exist between the compounds of a given type. It is certainly desirable to have these free-energy-temperature diagrams for as many types of compounds as are of present or potential use in metallurgical processes. Thus, even though there are but few uses of metallic fluorides in extractive metallurgy today, the potential uses of fluorine processes are of great importance and serve as the principal justification of this paper.

Recent developments in the production of fluorocarbons have resulted in vastly improved methods for the production and handling of fluorine and corrosive fluorides, with consequent reduction in costs.<sup>6,7</sup> The extractive metallurgist should no longer overlook possible fluorine processes when development of a new process for a relatively high unit-price metal is being considered.

In a previous paper<sup>8</sup> the author outlined in some detail the importance and use of free-energy data in metallurgical calculations and also discussed the properties of a standard free-energy vs. temperature diagram. The same method of presentation is adopted in this paper, and the reader is referred to the earlier work for explanations of the use of free-energy data.

## Thermodynamic Data

This paper presents standard free-energy vs. temperature diagrams, Figs. 1 and 2, for those fluorides for which the major thermodynamic constants are known. In the calculations of the standard free-energy of formation ( $\Delta G^\circ$ ), values of the enthalpy of formation at 298°K ( $\Delta H^\circ_f$ ) were taken from "Selected Values of Thermodynamic Constants",<sup>8</sup> most of the values of standard entropy at 298°K ( $S^\circ_{298}$ ) were taken from "Selected Values",<sup>8</sup> but in a few cases the values given by Kelley<sup>9</sup> were preferred; data for the phase changes came from "Selected Values" and several of Kelley's publica-

tions;<sup>9-12</sup> and most of the specific-heat data were taken from Kelley.<sup>10</sup> The appendix gives a detailed list of the sources of the data.

As explained in an earlier paper,<sup>8</sup> the accuracy of some of the standard free-energy relationships is not high. An error of  $\pm 1$  kcal at 1000°C is expected in most of the curves of Figs. 1 and 2. The error may be as high as  $\pm 3$  kcal in some of the curves. Rather than attempt to estimate the reliability of each curve, the source of the data used is reported in the appendix, and the reader may compare these data with newer values as they become available.

Figs. 1 and 2 fail to show values for the fluorides of many important metals. In most cases this is because the entropy of the metallic fluoride is unknown. For preliminary calculations it is often useful to have available the best estimate of an unknown datum, rather than no information at all. With this in mind, Table I lists estimated standard free-energy values for a number of important metallic fluorides not included in Figs. 1 and 2. The values reported in Table I were calculated by Brewer et al.<sup>13</sup> and are based on estimated entropy values. The estimated uncertainty of the values for each fluoride were calculated from the uncertainty values given by Brewer<sup>13</sup> for  $\Delta H^\circ$ , and the entropy function.

Table I. Estimated Values of Standard Free Energy of Fluorides\*

| Compound             | Temp. °C |        |        |            | Uncertainty, kcal at |       |
|----------------------|----------|--------|--------|------------|----------------------|-------|
|                      | 25°      | 227°   | 727°   | 1227°      | 227°C                | 727°C |
| 2AuF                 | — 28.2   | — 23.0 | — 18.0 |            | 9                    | 13    |
| 2HgF                 | — 79.4   | — 70.0 |        |            | 15                   |       |
| HgF <sub>2</sub>     | — 83.1   | — 74.5 |        |            | 10                   |       |
| 2CuF                 | —110.4   | —104.0 | — 92.0 | — 78.0 (1) | 8                    | 12    |
| 2/3 CoF <sub>3</sub> | —116.1   | —109.0 | — 93.4 |            | 7                    | 9     |
| CuF <sub>2</sub>     | —117.6   | —110.5 | — 95.0 |            | 5                    | 6     |
| 2/3 BiF <sub>3</sub> | —133.3   | —125.7 |        |            | 6                    |       |
| 2/3 SbF <sub>3</sub> | —135.3   | —128.8 |        |            | 4                    |       |
| 2/3 FeF <sub>3</sub> | —146.0   | —138.2 | —122.0 | —106.7 (1) | 9                    | 10    |
| NiF <sub>2</sub>     | —147.3   | —140.0 | —124.0 | —108.5     | 3                    | 5     |
| CoF <sub>2</sub>     | —147.9   | —141.0 | —125.0 | —108.5 (1) | 3                    | 5     |
| 2/3 MnF <sub>3</sub> | —148.1   | —141.0 |        |            | 4                    |       |
| SnF <sub>2</sub>     | —148.5   | —141.5 |        |            | 5                    |       |
| FeF <sub>2</sub>     | —157.6   | —150.5 | —133.0 | —118.5 (1) | 3                    | 5     |
| ZnF <sub>2</sub>     | —165.6   | —158.5 | —142.0 |            | 4                    | 6     |
| 2/3 CrF <sub>3</sub> | —166.7   | —159.3 | —143.3 | —131.3 (1) | 4                    | 6     |
| CrF <sub>2</sub>     | —171.9   | —165.5 | —148.0 | —137.0 (1) | 4                    | 6     |
| 1/2 TiF <sub>4</sub> | —175.2   | —167.8 |        |            | 10                   |       |
| 1/2 ZrF <sub>4</sub> | —211.5   | —204.0 | —187.5 |            | 15                   | 16    |
| BeF <sub>2</sub>     | —216.9   | —210.5 | —195.0 | —183.5 (1) | 5                    | 6     |

\* Based on values estimated by Brewer et al.<sup>13</sup> Values are for the solid compounds, except those marked (1), which are for the liquid fluorides. Uncertainty values take into account the uncertainty in  $\Delta S^\circ$  as well as  $\Delta H^\circ$ .

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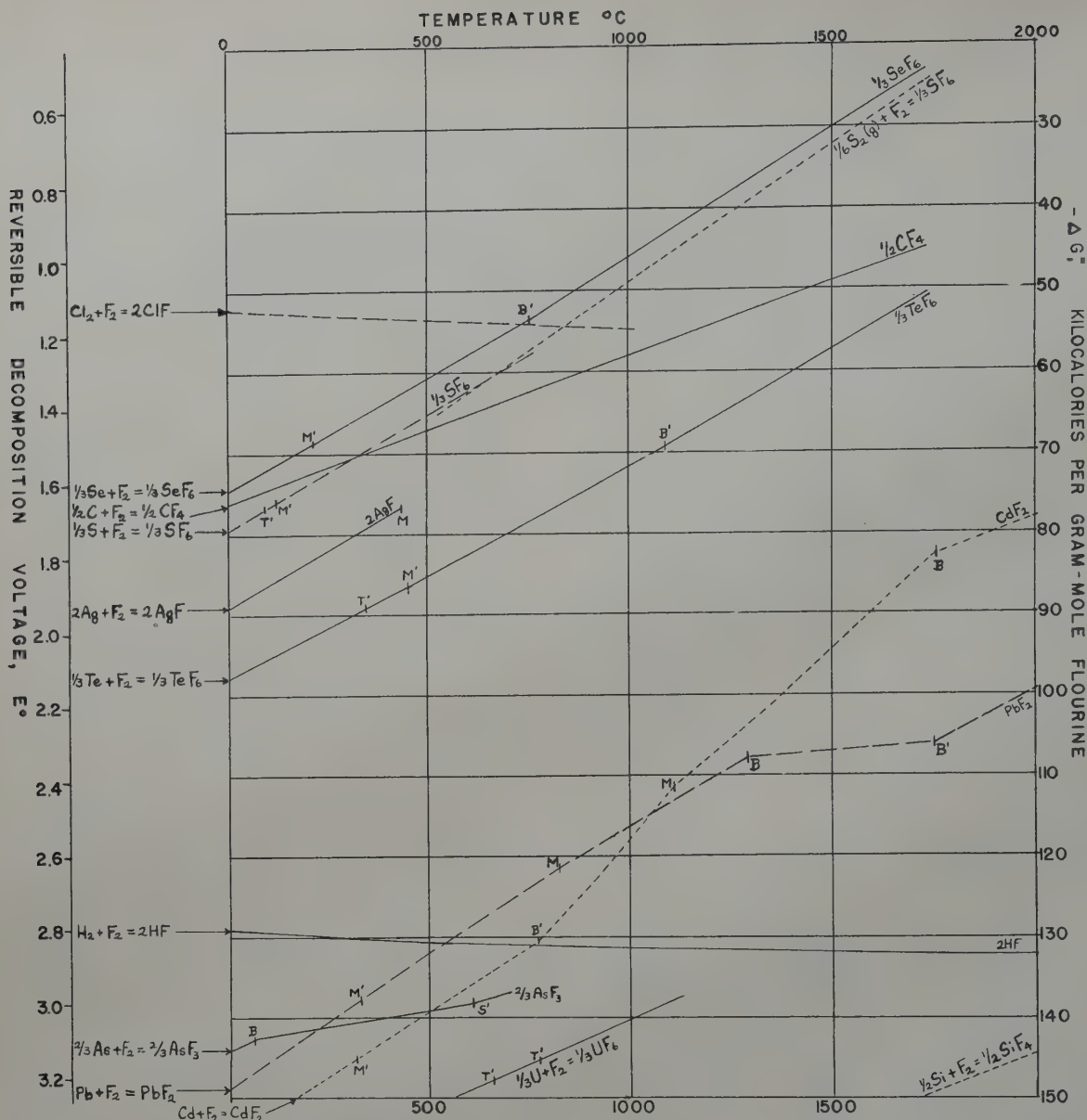


Fig. 1—Standard free energies of formation for metal fluorides as a function of temperature  $\Delta G^\circ$  between  $-20$  and  $-150$  kcal.

*M, B, S, and T* refer to normal melting, boiling, sublimation, and transition temperatures of the metal fluorides; *M', B', S', and T'* refer to the same phase changes for the metal.

### Metallurgical Applications

**Reduction of Fluorides:** It will be recalled<sup>5</sup> that a free-energy vs. temperature diagram such as given in Figs. 1 and 2, is a quantitative affinity series for the compounds listed, which is valid over the temperature range covered. The most stable fluorides are those with the most negative value of the standard free-energy of formation (the alkali and alkaline-earth fluorides at the bottom of Fig. 2). Since the basis for the values reported on Figs. 1 and 2 is 1 mol of fluorine, the subtraction of the value for one fluoride from that of another fluoride, results in the reaction whereby the latter metal replaces the former fluoride to yield the latter fluoride and the former metal. The standard free-energy for this replacement reaction, at any given temperature, is the algebraic sum of the standard free-energies read from Figs. 1 and 2. A negative value for the standard free-energy of any reaction indicates that the reaction is spontaneous when all of the reactants and products are in their standard states.

The positions of the curves on Figs. 1 and 2 (and the data of Table I) show at a glance the possibilities for hydrogen reduction of any given fluoride. The metallic fluorides whose curves lie above the curve for  $2\text{HF}$  can be reduced to the metal by hydrogen gas under standard conditions. As the temperature increases the reduction by hydrogen becomes more spontaneous.

A fluoride such as  $\text{UF}_6$ , whose curve lies slightly below the  $2\text{HF}$  curve at  $1000^\circ\text{C}$  can be reduced to the metal with hydrogen if the partial pressure of  $\text{H}_2$  is kept high and that of  $\text{HF}$  low, so that the free-energy ( $\Delta G$ ) becomes negative, even though the standard free-energy ( $\Delta G^\circ$ ) is positive (see ref. 5 for details of calculation of  $\Delta G$  from  $\Delta G^\circ$ ). The fluorides whose curves lie far below the  $2\text{HF}$  curve cannot be reduced to the metal by hydrogen under practical conditions.

As with the chlorides, carbon is almost valueless as a reducing agent for metal fluorides. This conclusion is based on the position of the curve for  $\text{CF}_4$ , which lies far above the curves for most of the



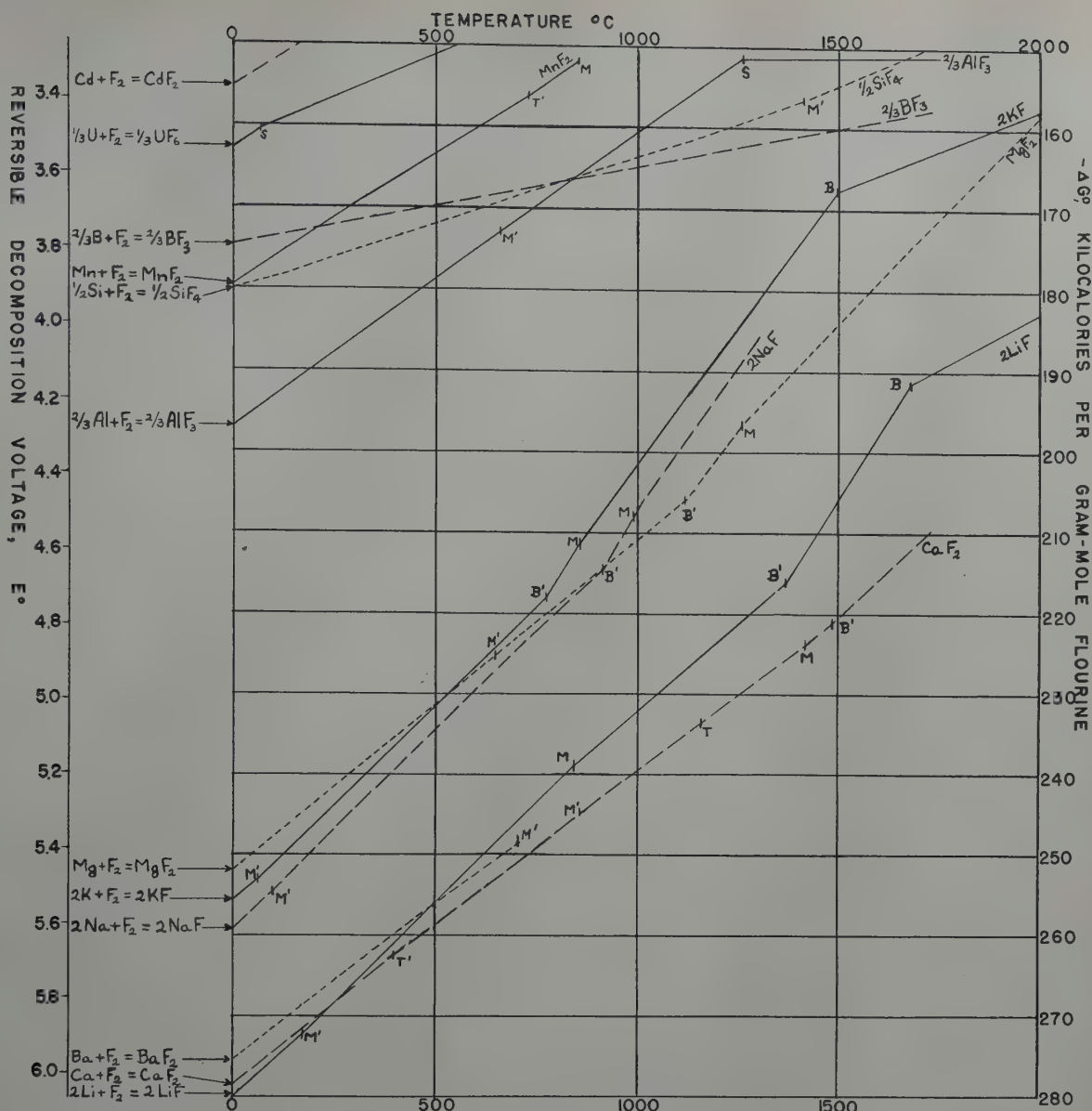


Fig. 2—Standard free energies of formation for metal fluorides as a function of temperature  $\Delta G^\circ$  between  $-150$  and  $280$  kcal.

*M, B, S, and T* refer to normal melting, boiling, sublimation, and transition temperatures of the metal fluorides; *M', B', S', and T'* refer to the same phase changes for the metal.

other fluorides. Sulphur, selenium, and tellurium are likewise very poor reducing agents for most of the fluorides.

A metal will act as a reducing agent for another metal fluoride, if the curve for the fluoride of the reducing agent lies below the curve for the fluoride to be reduced. Thus, magnesium metal could be used to reduce  $\text{TiF}_4$ ,  $\text{ZrF}_4$ ,  $\text{SiF}_4$ , etc., in analogy to the Kroll process.<sup>14</sup>

By adjustment of conditions far from the standard states, such as by use of a vacuum process, the direction of many reduction reactions can be reversed. Thus, silicon metal could be used to reduce aluminum fluoride to the metal at  $700^\circ\text{C}$ , even though the curve for  $\text{SiF}_4$  lies above the curve for  $\text{AlF}_3$  and  $\Delta G^\circ$  for the reduction reaction is positive.



$$\Delta G^\circ_{700^\circ\text{C}} = +171,400 - 168,400 = +3,000 \text{ cal}$$

$$K_{700^\circ\text{C}} = 0.212$$

If, for a first approximation, the aluminum and

silicon are assumed to remain as pure metals, then:

$$K_{700^\circ\text{C}} = 0.212 = \frac{P_{\text{SiF}_4}^{1/2} \times 1}{1 \times 1}$$

$$P_{\text{SiF}_4} = 0.045 \text{ atm} = 34 \text{ mm of Hg}$$

If the reaction were carried out in a vacuum retort, and the pressure kept lower than 34 mm of Hg, the reaction would proceed spontaneously from left to right provided the reaction rate was sufficiently great. For more accurate calculations the alloying of aluminum and silicon would have to be considered.

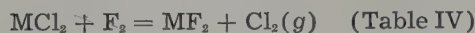
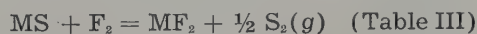
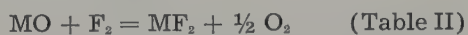
Electrolysis can be used to reduce any of the fluorides to the metal and fluorine. Figs. 1 and 2 show the reversible decomposition voltage for the electrolysis of the pure fluoride to produce pure metal and fluorine at 1 atm pressure. When the fluoride bath is a mixture of fluorides, appropriate activity corrections must be made to obtain the reversible decomposition voltage under nonstandard conditions (see ref. 5).

In any reaction involving several fluorides, the

possible formation of double fluorides, of which cryolite ( $3\text{NaF} \cdot \text{AlF}_3$ ) is an example, must be taken into account. Kroll<sup>15</sup> has reported the relative stability of several double fluorides and has shown their importance in fluorine metallurgy. The formation of a double fluoride has the effect of reducing the activity of the individual fluorides in a degree proportional to the stability of the double fluoride.

### Fluorination of Oxides, Sulphides, and Chlorides

Tables II, III, and IV list standard free-energies for the type reactions:

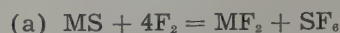


The negative values for  $\Delta G^\circ$  exhibited by all of the reactions in Tables II, III, and IV, indicate that all oxides, sulphides, and chlorides can be fluorinated by fluorine gas under standard conditions. This conclusion emphasizes the unusual stability of the

fluorides—they are the most stable general class of compounds.

Despite the fact that the metals and oxides are all thermodynamically unstable with respect to fluorine gas, many metals and certain oxides do not react with dry fluorine gas at room temperature and even higher, because of extremely low reaction rate. Dry fluorine can be handled in glass or silica apparatus at room temperature and somewhat above.<sup>6</sup> Dry fluorine does not appreciably attack steel at 200°C or nickel at 600°C.

When fluorinating a sulphide or chloride with an excess of fluorine gas, the reaction will proceed to the formation of  $\text{SF}_6$  and  $\text{ClF}$ , rather than releasing  $\text{S}_2$  and  $\text{Cl}_2$  as indicated in Tables III and IV, provided that the reaction rate for the formation of  $\text{SF}_6$  or  $\text{ClF}$  is sufficient at the temperature in question. Thus, the complete reactions will be:



$\Delta G^\circ$  for reaction (a) will be more negative (the reaction is more spontaneous) than the values reported in Table III by 198 kcal at 500°C and 147 kcal at 1000°C. The value of  $\Delta G^\circ$  for reaction (b) will be more negative than the values reported in Table IV by 53.5 kcal at 500°C and 54.8 kcal at 1000°C.

If a limited amount of fluorine gas is used to fluorinate a metal sulphide or chloride, the metal fluoride will be produced rather than the sulphur fluoride or chlorine fluoride, as indicated by the relative stability of the fluorides on Figs. 1 and 2.

Tables II, III, and IV also serve to show standard free-energies of fluorination of the oxides, sulphides, and chlorides by other fluorides. The standard free-energy of fluorination of an oxide by HF is obtained by subtracting eq 3 (Table II) from the equation for

Table II. Fluorination of Oxides by Fluorine Gas\*

| Number | Reaction                                                                                             | $\Delta G^\circ$ in kilo-calories |        |        |
|--------|------------------------------------------------------------------------------------------------------|-----------------------------------|--------|--------|
|        |                                                                                                      | 25°                               | 500°   | 1000°  |
| 1      | $\frac{1}{2} \text{CO}_2 + \text{F}_2 = \frac{1}{2} \text{CF}_4 + \frac{1}{2} \text{O}_2$            | -28.7                             | -19.8  | -10.8  |
| 2†     | $\frac{1}{2} \text{TiO}_2 + \text{F}_2 = \frac{1}{2} \text{TiF}_4 + \frac{1}{2} \text{O}_2$          | -72.6                             |        |        |
| 3      | $\text{H}_2\text{O} + \text{F}_2 = 2\text{HF} + \frac{1}{2} \text{O}_2$                              | -74.1                             | -81.8  | -89.3  |
| 4      | $\frac{1}{3} \text{Al}_2\text{O}_3 + \text{F}_2 = \frac{2}{3} \text{AlF}_3 + \frac{1}{2} \text{O}_2$ | -74.2                             | -67.0  | -59.9  |
| 5†     | $\text{Cu}_2\text{O} + \text{F}_2 = 2\text{CuF} + \frac{1}{2} \text{O}_2$                            | -75.0                             | -68.6  | -63.7  |
| 6      | $\frac{1}{2} \text{SiO}_2 + \text{F}_2 = \frac{1}{2} \text{SiF}_4 + \frac{1}{2} \text{O}_2$          | -82.0                             | -84.4  | -86.9  |
| 7†     | $\frac{1}{3} \text{Cr}_2\text{O}_3 + \text{F}_2 = \frac{2}{3} \text{CrF}_3 + \frac{1}{2} \text{O}_2$ | -83.6                             | -77.0  | -73.1  |
| 8      | $\text{Ag}_2\text{O} + \text{F}_2 = 2\text{AgF} + \frac{1}{2} \text{O}_2$                            | -86.2                             |        |        |
| 9†     | $\frac{1}{2} \text{ZrO}_2 + \text{F}_2 = \frac{1}{2} \text{ZrF}_4 + \frac{1}{2} \text{O}_2$          | -89.0                             | -81.6  |        |
| 10†    | $\text{ZnO} + \text{F}_2 = \text{ZnF}_2 + \frac{1}{2} \text{O}_2$                                    | -89.9                             | -85.2  |        |
| 11     | $\text{MnO} + \text{F}_2 = \text{MnF}_2 + \frac{1}{2} \text{O}_2$                                    | -92.0                             | -84.7  |        |
| 12†    | $\text{NiO} + \text{F}_2 = \text{NiF}_2 + \frac{1}{2} \text{O}_2$                                    | -94.7                             | -88.7  | -83.5  |
| 13†    | $\text{CoO} + \text{F}_2 = \text{CoF}_2 + \frac{1}{2} \text{O}_2$                                    | -97.2                             | -89.6  | -82.2  |
| 14     | $\text{CdO} + \text{F}_2 = \text{CdF}_2 + \frac{1}{2} \text{O}_2$                                    | -97.5                             | -95.4  | -94.6  |
| 15     | $\frac{1}{3} \text{As}_2\text{O}_3 + \text{F}_2 = \frac{2}{3} \text{AsF}_3 + \frac{1}{2} \text{O}_2$ | -98.2                             | -101.1 |        |
| 16†    | $\text{FeO} + \text{F}_2 = \text{FeF}_2 + \frac{1}{2} \text{O}_2$                                    | -100.0                            | -90.5  | -81.7  |
| 17     | $\text{PbO} + \text{F}_2 = \text{PbF}_2 + \frac{1}{2} \text{O}_2$                                    | -103.0                            | -96.8  | -90.8  |
| 18     | $\text{MgO} + \text{F}_2 = \text{MgF}_2 + \frac{1}{2} \text{O}_2$                                    | -112.4                            | -103.8 | -96.6  |
| 19     | $\text{CaO} + \text{F}_2 = \text{CaF}_2 + \frac{1}{2} \text{O}_2$                                    | -133.3                            | -125.5 | -118.4 |
| 20     | $\text{BaO} + \text{F}_2 = \text{BaF}_2 + \frac{1}{2} \text{O}_2$                                    | -148.9                            | -141.0 |        |
| 21     | $\text{Na}_2\text{O} + \text{F}_2 = 2\text{NaF} + \frac{1}{2} \text{O}_2$                            | -169.1                            | -159.7 | -151.3 |
| 22     | $\text{K}_2\text{O} + \text{F}_2 = 2\text{KF} + \frac{1}{2} \text{O}_2$                              | -179.1                            | -170.9 |        |

\* Data for fluorides from Figs. 1 and 2 and Table I. Data for  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{FeO}$ , from Richardson and Jeffes.<sup>3</sup> Data for  $\text{Ag}_2\text{O}$ ,  $\text{CdO}$ , from Dannatt and Ellingham.<sup>2</sup> Data for  $\text{NiO}$ ,  $\text{ZnO}$ ,  $\text{PbO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{ZrO}_2$  from Osborn.<sup>4</sup> Standard states are  $\text{F}_2(\text{g})$  and  $\text{O}_2(\text{g})$  at 1 atm, and the forms of the oxide and fluoride which are stable (at 1 atm pressure) at the temperature in question.

† Based on estimated value for standard free-energy of formation of the fluoride.

Table III. Fluorination of Sulphides by Fluorine Gas\*

| Number | Reaction                                                                                  | $\Delta G^\circ$ in kilo-calories |        |        |
|--------|-------------------------------------------------------------------------------------------|-----------------------------------|--------|--------|
|        |                                                                                           | 25°                               | 500°   | 1000°  |
| 1      | $\frac{1}{2} \text{CS}_2 + \text{F}_2 = \frac{1}{2} \text{CF}_4 + \frac{1}{2} \text{S}_2$ | -73.6                             | -64.9  | -55.7  |
| 2†     | $\text{Cu}_2\text{S} + \text{F}_2 = 2\text{CuF} + \frac{1}{2} \text{S}_2$                 | -80.9                             | -73.1  | -64.2  |
| 3†     | $\text{ZnS} + \text{F}_2 = \text{ZnF}_2 + \frac{1}{2} \text{S}_2$                         | -108.5                            | -103.2 |        |
| 4      | $\text{H}_2\text{S} + \text{F}_2 = 2\text{HF} + \frac{1}{2} \text{S}_2$                   | -111.4                            | -118.3 | -124.9 |
| 5      | $\text{CdS} + \text{F}_2 = \text{CdF}_2 + \frac{1}{2} \text{S}_2$                         | -111.6                            | -106.3 | -102.5 |
| 6      | $\text{PbS} + \text{F}_2 = \text{PbF}_2 + \frac{1}{2} \text{S}_2$                         | -115.7                            | -108.7 | -103.3 |
| 7†     | $\text{NiS} + \text{F}_2 = \text{NiF}_2 + \frac{1}{2} \text{S}_2$                         | -116.7                            | -106.6 | -97.9  |
| 8†     | $\text{FeS} + \text{F}_2 = \text{FeF}_2 + \frac{1}{2} \text{S}_2$                         | -125.1                            | -114.3 | -105.0 |
| 9†     | $\text{MnS} + \text{F}_2 = \text{MnF}_2 + \frac{1}{2} \text{S}_2$                         | -139.4                            | -131.2 |        |
| 10     | $\text{CaS} + \text{F}_2 = \text{CaF}_2 + \frac{1}{2} \text{S}_2$                         | -158.0                            | -149.9 | -142.2 |

\* Data for fluorides from Figs. 1 and 2 and Table I. Data for  $\text{CdS}$ ,  $\text{FeS}$ ,  $\text{Cu}_2\text{S}$ , and  $\text{CS}_2$  from Dannatt and Ellingham.<sup>2</sup> Data for  $\text{ZnS}$ ,  $\text{H}_2\text{S}$ ,  $\text{PbS}$ ,  $\text{NiS}$ ,  $\text{MnS}$ , and  $\text{CaS}$  from Osborn.<sup>4</sup> Standard states are  $\text{F}_2(\text{g})$  and  $\text{S}_2(\text{g})$  at 1 atm, and the forms of the sulphide and fluoride which are stable (at 1 atm pressure) at the temperature in question.

† Based on estimated value for standard free-energy of formation of the fluoride.

Table IV. Fluorination of Chlorides by Fluorine Gas\*

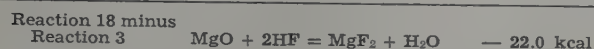
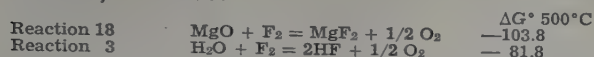
| Number | Reaction                                                                                              | $\Delta G^\circ$ in kilo-calories |        |        |
|--------|-------------------------------------------------------------------------------------------------------|-----------------------------------|--------|--------|
|        |                                                                                                       | 25°                               | 500°   | 1000°  |
| 1      | $2\text{AgCl} + \text{F}_2 = 2\text{AgF} + \text{Cl}_2$                                               | -36.1                             |        |        |
| 2†     | $\text{HgCl}_2 + \text{F}_2 = \text{HgF}_2 + \text{Cl}_2$                                             | -39.3                             |        |        |
| 3†     | $\text{Cu}_2\text{Cl}_2 + \text{F}_2 = 2\text{CuF} + \text{Cl}_2$                                     | -54.0                             | -53.5  | -51.1  |
| 4      | $\frac{1}{2} \text{C Cl}_4 + \text{F}_2 = \frac{1}{2} \text{CF}_4 + \text{Cl}_2$                      | -67.5                             | -67.5  |        |
| 5      | $\text{CdCl}_2 + \text{F}_2 = \text{CdF}_2 + \text{Cl}_2$                                             | -72.7                             | -74.2  | -71.9  |
| 6      | $\text{PbCl}_2 + \text{F}_2 = \text{PbF}_2 + \text{Cl}_2$                                             | -73.0                             | -73.4  | -68.2  |
| 7      | $\frac{2}{3} \text{AlCl}_3(\text{g}) + \text{F}_2 = \frac{2}{3} \text{AlF}_3(\text{s}) + \text{Cl}_2$ |                                   |        | -69.3  |
| 8      | $\text{MnCl}_2 + \text{F}_2 = \text{MnF}_2 + \text{Cl}_2$                                             | -73.2                             | -72.7  |        |
| 9      | $2\text{NaCl} + \text{F}_2 = 2\text{NaF} + \text{Cl}_2$                                               | -74.4                             | -71.7  | -66.6  |
| 10†    | $\text{SnCl}_2 + \text{F}_2 = \text{SnF}_2 + \text{Cl}_2$                                             | -75.6                             |        |        |
| 11†    | $\text{ZnCl}_2 + \text{F}_2 = \text{ZnF}_2 + \text{Cl}_2$                                             | -77.2                             | -75.4  |        |
| 12†    | $\text{CoCl}_2 + \text{F}_2 = \text{CoF}_2 + \text{Cl}_2$                                             | -80.3                             | -80.3  | -77.4  |
| 13†    | $\text{NiCl}_2 + \text{F}_2 = \text{NiF}_2 + \text{Cl}_2$                                             | -82.2                             | -81.8  | -81.4  |
| 14†    | $\frac{2}{3} \text{BiCl}_3 + \text{F}_2 = \frac{2}{3} \text{BiF}_3 + \text{Cl}_2$                     | -82.5                             |        |        |
| 15     | $2\text{HCl} + \text{F}_2 = 2\text{HF} + \text{Cl}_2$                                                 | -83.6                             | -83.1  | -82.4  |
| 16†    | $\frac{2}{3} \text{SbCl}_3 + \text{F}_2 = \frac{2}{3} \text{SbF}_3 + \text{Cl}_2$                     | -83.7                             |        |        |
| 17†    | $\text{FeCl}_3 + \text{F}_2 = \text{FeF}_3 + \text{Cl}_2$                                             | -85.3                             | -83.0  | -76.5  |
| 18†    | $\text{CrCl}_3 + \text{F}_2 = \text{CrF}_3 + \text{Cl}_2$                                             | -86.4                             | -84.9  | -81.7  |
| 19†    | $\frac{1}{2} \text{TiCl}_4 + \text{F}_2 = \frac{1}{2} \text{TiF}_4 + \text{Cl}_2$                     | -93.5                             |        |        |
| 20     | $\frac{1}{3} \text{Al}_2\text{Cl}_6 + \text{F}_2 = \frac{2}{3} \text{AlF}_3 + \text{Cl}_2$            | -94.6                             | -85.3  |        |
| 21     | $\frac{2}{3} \text{AsCl}_3 + \text{F}_2 = \frac{2}{3} \text{AsF}_3 + \text{Cl}_2$                     | -96.1                             | -96.7  |        |
| 22     | $\text{CaCl}_2 + \text{F}_2 = \text{CaF}_2 + \text{Cl}_2$                                             | -97.7                             | -95.0  | -90.9  |
| 23†    | $\frac{1}{2} \text{ZrCl}_4 + \text{F}_2 = \frac{1}{2} \text{ZrF}_4 + \text{Cl}_2$                     | -107.2                            | -102.9 |        |
| 24     | $\text{MgCl}_2 + \text{F}_2 = \text{MgF}_2 + \text{Cl}_2$                                             | -109.4                            | -107.9 | -102.8 |
| 25     | $\frac{1}{2} \text{SiCl}_4 + \text{F}_2 = \frac{1}{2} \text{SiF}_4 + \text{Cl}_2$                     | -111.1                            | -111.4 | -111.0 |
| 26     | $\frac{2}{3} \text{BCl}_3 + \text{F}_2 = \frac{2}{3} \text{BF}_3 + \text{Cl}_2$                       | -113.6                            | -112.8 | -111.7 |
| 27†    | $\text{BeCl}_2 + \text{F}_2 = \text{BeF}_2 + \text{Cl}_2$                                             | -116.1                            |        |        |

\* Data for fluorides from Figs. 1 and 2 and Table I. Data for chlorides from Kellogg.<sup>5</sup> Standard states are  $\text{F}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  at 1 atm, and the forms of the chloride and fluoride which are stable (at 1 atm pressure) at the temperature in question.

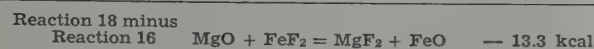
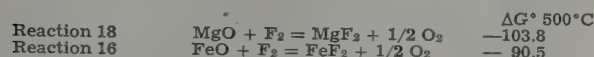
† Based on estimated value for the standard free-energy of formation of the fluoride.



the oxide. Thus, for the fluorination of MgO by HF at 500°C, we have:



And for fluorination of MgO by  $\text{FeF}_2$ , we have:



In general, fluorination of an oxide by a fluoride will be spontaneous, under standard conditions, if the equation for the oxide on Table II has a more negative value of  $\Delta G^\circ$ , than does the equation for the fluorinating agent. Thus, the fluorides at the top of Table II are the strongest fluorinating agents.

The free-energy of fluorination of sulphides and chlorides by metal fluorides can be derived from Tables III and IV in a similar manner.

One interesting application of the fluorination of oxides by hydrogen fluoride is afforded by the phosphate processing industry. In the thermal processing of phosphate rock to produce fused tricalcium phosphate, the fluorine content of the rock is driven off as hydrogen fluoride and enters the stack gases. A process for the recovery of the hydrogen fluoride from stack gases has recently been described.<sup>16</sup> The essential feature of the process is the reaction of the HF with a bed of crushed limestone at room temperature. The reaction is:



The standard free-energy of this reaction at 25°C can be obtained by combination of the data of Table II with the data on the decomposition of  $\text{CaCO}_3$  given by Osborn.<sup>4</sup> The result is:

$$\Delta G^\circ_{25^\circ\text{C}} \text{ for reaction (a)} = -28,100 \text{ cal.}$$

The reaction is therefore spontaneous under standard conditions, and the reaction rate is fast enough to allow efficient absorption of the HF.<sup>16</sup>

When producing superphosphate the evolved fluorine is principally in the form of  $\text{SiF}_4$ ,<sup>17</sup> and it is interesting to see whether limestone could be used to absorb this gas. The reaction would be:



Combination of the data of Table II with that of Osborn<sup>4</sup> yields:

$$\Delta G^\circ_{25^\circ\text{C}} \text{ for reaction (b)} = -20,200$$

This reaction is also spontaneous at room temperature; its rate characteristics have not been reported.

### Summary

The uses of fluorine and fluorides in extractive metallurgy today are very few. However, it is reasonable to expect that the increased "know-how" in handling of fluorine and fluorides, the availability of large quantities of fluorine at relatively low prices, and the unusual properties of many of the metallic fluorides will result in new metallurgical processes.

The free-energy values reported in this paper can serve as a valuable tool in any exploratory work in fluorine metallurgy. The importance and use of thermodynamic data in metallurgical calculations have not been discussed in this paper, but will be

found in an earlier paper,<sup>5</sup> or in any textbook on thermodynamics.

### Acknowledgment

The author is indebted and grateful to Jane Breckwoltdt, Research Associate in Mineral Engineering, who performed duplicate calculations for all the material shown on Figs. 1 and 2.

### Appendix

#### Sources of Thermodynamic Data for Figs. 1 and 2

Numbers refer to references at end of paper

| Fluoride         |                         |               |                 | Metal           |               |                 |
|------------------|-------------------------|---------------|-----------------|-----------------|---------------|-----------------|
| $S^\circ_{298}$  | $\Delta H^\circ_{f298}$ | Phase Changes | Specific Heat   | $S^\circ_{298}$ | Phase Changes | Specific Heat   |
| AgF              | 8                       | 8             | a               | 8               | 10            | 10              |
| AlF <sub>3</sub> | 8                       | 8             | 10 <sup>b</sup> | 8               | 10            | 10              |
| AsF <sub>3</sub> | 8                       | 8             | 8,10            | 8               | 8             | 10 <sup>c</sup> |
| BF <sub>3</sub>  | 8                       | 8             | 10              | 8               |               | 10              |
| BaF <sub>2</sub> | 9                       | 8             | 10              | 9               |               | 10              |
| CF <sub>4</sub>  | 8                       | 8             | 10              | 8               |               | 10              |
| CaF <sub>2</sub> | 9                       | 8             | 10              | 9               | 10,11,12      | 10,12           |
| CdF <sub>2</sub> | 8                       | 8             | 8               | 8               | 8             | 10,12           |
| ClF              | 9                       | 8             | f               | 8               |               | f               |
| HF               | 8                       | 8             | 10              | 8               |               | 10              |
| KF               | 18                      | 8             | 10,12           | 9               | 10,12         | 10,12           |
| LiF              | 9                       | 8             | 8               | 8               | 8,12          | 10,12           |
| MgF <sub>2</sub> | 8                       | 8             | 10              | 8               | 8             | 10,12           |
| MnF <sub>2</sub> | 8                       | 8             | a               | 8               | 8             | 10              |
| NaF              | 9                       | 8             | 10,12           | 9               | 10,12         | 10,12           |
| PbF <sub>2</sub> | 8                       | 8             | 8               | 8               | 8             | 10,12           |
| SF <sub>6</sub>  | 8                       | 8             | 10              | 8,9             | 10,8          | 10              |
| SeF <sub>6</sub> | 8                       | 8             | 10              | 8               | 8             | 10              |
| SiF <sub>4</sub> | 8                       | 8             | 10              | 8               | 8             | 10              |
| TeF <sub>6</sub> | 8                       | 8             | 10              | 8               | 8             | 10 <sup>d</sup> |
| UF <sub>6</sub>  | 8                       | 8             | 19              | 8               | 10            | 10              |

<sup>a</sup> Estimated.

<sup>b</sup> Neglect  $\Delta C_p$  above 1530°K.

<sup>c</sup> Neglect  $\Delta C_p$  above 883°K.

<sup>d</sup> Estimated  $C_p$  for liquid.

<sup>e</sup> Estimated  $C_p$  for liquid and gaseous forms.

<sup>f</sup> Neglect  $\Delta C_p$ .

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## Cobalt Self-Diffusion:

# A Study of the Method Of Decrease in Surface Activity

by R. C. Ruder and

C. E. Birchenall

The method of decrease in surface activity was used to determine the rates of diffusion of  $\text{Co}^{60}$  into cobalt and into nickel. Since the absorption curves for cobalt radiation were quite complex under the conditions of these experiments, the effects of geometry and surface preparation on the diffusion results were investigated. The cobalt self-diffusion coefficients obey the equation

$$D_{\text{Co}}^{\text{Co}} = e^{-61900/RT} \text{ cm}^2 \text{ per sec.}$$

For dilute cobalt diffusing in nickel,

$$D_{\text{Ni}}^{\text{Co}} = 1.46 e^{-68800/RT} \text{ cm}^2 \text{ per sec.}$$

AS part of the general program to measure the self-diffusion and dilute-solution diffusion rates of the iron-group metals, the diffusion coefficients of cobalt into cobalt and nickel have been measured using the radioactive isotope  $\text{Co}^{60}$ . Self-diffusion studies in iron have been previously reported by Birchenall and Mehl.<sup>1</sup> The technique of measurement used was the decrease in surface activity method described by Steigman, Shockley, and Nix.<sup>2</sup> It has been determined that scattering of the measured beta radiation by the specimen matrix is significantly influenced by the condition of the surface and the counting geometry. Accurate diffusion coefficients can be calculated from the activity data provided that the specimens have plane diffusion surfaces and that the absorption properties of the emitted radiation are determined under geometrical

conditions duplicating with external absorbers the absorption and scattering in a thin film at the specimen surface as nearly as possible.

The cobalt used in this research was originally in the form of hydrogen reduced rondels 99.9+ pct pure. The nickel had been prepared by the carbonyl process and was found by spectrographic analysis to contain 0.03 pct Fe, 0.04 pct Co and smaller traces of other metallic elements for a balance purity of 99.9+ pct Ni. Both materials were vacuum melted and cast in rectangular ingots. Specimens  $\frac{7}{8} \times \frac{7}{8} \times \frac{1}{4}$  in. were machined from these ingots. The specimens were then ground to 4-0 emery paper and annealed in hydrogen for at least a day at 1200°C. Some of the specimens were used in preliminary experimentation after which their diffusion faces were machined to remove the radioactive material from the previous diffusion experiments. After grinding, the specimens were polished using an electrolytic lapping technique described by Mazia.<sup>3</sup> This lapping was continued until at least 0.005 in. was removed from the diffusion surface. The final surfaces were metallographically smooth except for a few fine scratches caused by the glass cloth. A large percentage of the area was undisturbed as determined by microscopic examination.

The grain diameters of the diffusion specimens varied from 0.1 to 5 mm. There were no effects due to grain boundary diffusion in the experiments

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This paper represents part of a thesis submitted by R. C. Ruder in partial fulfillment of requirements for the degree of Doctor of Science to the Graduate Committee of the Carnegie Institute of Technology.



reported here. Probably none should be expected for the grain sizes and temperatures employed.

Cobalt, containing radioactive  $\text{Co}^{60}$ , was plated on the diffusion surfaces from a cobalt sulphate solution made slightly basic with ammonium hydroxide. From specific activity calculations the plated film was of the order of  $10^{-7}$  cm thick. The active cobalt was removed from the edges of the specimens and from the diffusion surfaces for a distance of at least  $\frac{1}{8}$  in. from the edge. Each diffusion experiment consisted of two specimens placed in an iron boat with their diffusion faces together in order to minimize the loss of the active cobalt through evaporation during the high-temperature anneal. Autoradiographs were made of the diffusion surfaces before and after the diffusion anneals. There was no evidence of any change in the surface distribution of the activity due either to evaporation or surface diffusion. Lateral diffusion was too small to produce a significant change in geometry.

The diffusion anneals were carried out in an atmosphere of hydrogen from which oxygen was removed by hot platinized asbestos, followed by drying over activated alumina. In addition, the presence of powdered iron and the iron of the supporting boat removed the final traces of oxygen in the furnace tube. There was no visible oxidation of the diffusion specimens. The temperature was automatically controlled to  $\pm 2^\circ\text{C}$ . In addition, the furnace temperature close to the specimens was checked frequently during the diffusion experiments. The temperature of the specimens was recorded during the heating and cooling of the furnaces, and appropriate correction was made if there was appreciable diffusion occurring during these periods.

The specimens, having nearly equal activities, were counted before and after the diffusion anneals using an argon filled self-quenching tube mounted in a lead counting safe. Counting was continued for times long enough to reduce the statistical counting error well below 1 pct. Relative counting rates were calculated with reference to a standard specimen which was counted frequently during the activity measurements. Appropriate correction was made for background and coincidence errors. At least three counts were made on each specimen to reduce systematic errors in counting rate due to climatic conditions. Agreement within 1 pct was considered satisfactory. Absorption measurements, using nickel, aluminum, and cobalt absorbers, were made on individual specimens before and after diffusion and under various geometric conditions. Details will be considered later.

### Calculation of Diffusion Coefficient

Due to the form of the absorption curve, it is impossible to use an analytical method of computing the diffusion coefficient. A graphical integration was required. The diffusion of an infinitely thin layer of one atomic species into a semi-infinite solid of another may be represented by a function of the form:

$$C = \frac{C_0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

which is the solution of Fick's law appropriate to the boundary conditions, where  $C$  is the concentration of the first species of atom at a distance  $x$  from the diffusion interface.  $C_0$  is the total amount of the first species.  $D$  is the diffusion coefficient, and  $t$

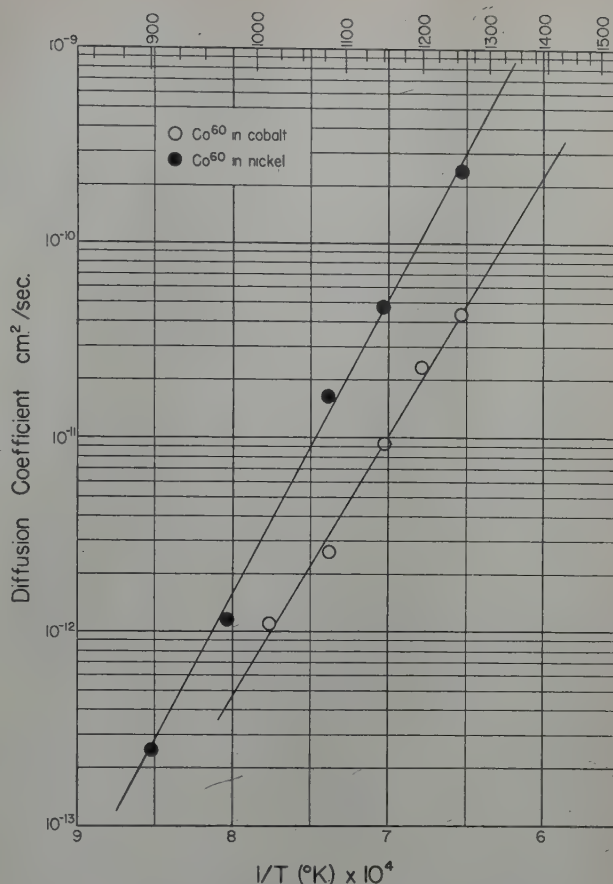


Fig. 1—Temperature dependence of diffusion coefficients for cobalt self-diffusion and for dilute cobalt diffusing in nickel.

is the time of the diffusion anneal. The distribution in  $x$  is therefore determined by the product  $Dt$ . The radiation detected at the surface of the specimen after diffusion from the active material at a distance  $x$  from the surface is obtained from the experimentally determined absorption curve. The ratio of the activities after and before diffusion is therefore the integral from the diffusion interface to a point effectively at an infinite distance into the specimen of the product of the concentration-distance function and the absorption-distance function, divided by the integral of the concentration-distance function. Since the activity ratio is a function of the  $Dt$  product, this graphical process was carried out for a number of  $Dt$  products, and the resulting function of activity ratio vs.  $Dt$  was used to calculate the diffusion coefficient by interpolation. Since this function is appropriate to the tracer and geometry used in these experiments only, it is not presented.

The results of these experiments are given in Fig. 1. The standard deviation of the plotted points from the best least square straight line is about 15 pct, which from calculated errors arising from the observed statistical distribution of the counting rates, errors in absorption measurement and variations in temperature measurement, may be considered satisfactory. For cobalt self-diffusion:

$$D = 0.032 \exp \left( \frac{61.9 \pm 3.5}{RT} \right) \text{ cm}^2 \text{ per sec}$$

while for very dilute cobalt diffusing into nickel:

$$D = 1.46 \exp \left( \frac{68.3 \pm 2.0}{RT} \right) \text{ cm}^2 \text{ per sec.}$$

Here the activation energies are expressed in kcal

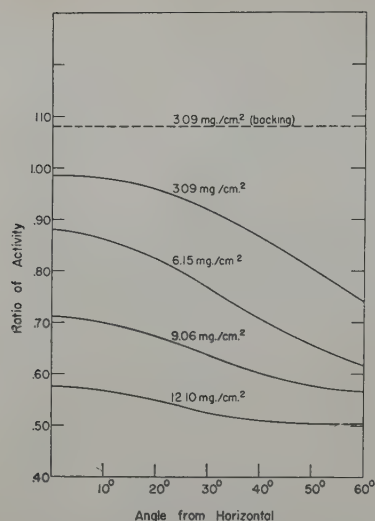


Fig. 2—Ratio of activity of a point source of  $\text{Co}^{60}$  under an absorber which makes an angle  $\theta$  with the horizontal plane to the activity of the same source under no absorber.

An exponential correction has been applied for the effectively greater thickness of the absorber due to rotation.

per mol. Cobalt does not show evidence of a change in the diffusion behavior at the Curie point. Nor is there a change at any other temperature in the measured range which might be considered as evidence of a high-temperature phase transformation.

### Absorption and Scattering of Beta Particles\*

An understanding of absorption and scattering processes is critical for the evaluation of diffusion data by the method of decrease in surface activity. Novey and Elliott<sup>5</sup> and Burt<sup>6</sup> found maxima in absorption curves when the source was some distance from the detector. The latter also found that the maxima disappeared if the absorbers were placed close to the counting tube rather than close to the source. Willard and Johnston<sup>7</sup> studied the effect of moving an absorber from tube window toward the source using both randomly directed and collimated radiation. The 1.69 mev. maximum energy beta radiation from  $\text{P}^{32}$  and the 1.1 and 1.3 mev. gamma rays from  $\text{Co}^{60}$  were used. When the radiation was collimated to allow detection of only those rays going directly from source to counter, the effect of moving the absorber from the tube toward the source was to decrease the counting rate for both gamma and beta radiation, though the effect was much stronger for betas. When the collimator was removed, permitting detection of particles scattered into the solid angle subtended by the tube although their original directions lay outside that angle, the effect of moving the absorber from the tube toward the source was to increase the counting rate about the same amount for both beta and gamma radiations.

These experiments rule out the possibility that the effect could be caused by the creation of secondary

radiation and give preliminary indication that the scattering effects are large and significant. The effects could be described in terms of a change in the angular distribution of the radiation as it passes through absorber which also acts as a scattering source. This change in angular distribution would be one in which the component of intensity of the radiation perpendicular to the plane of the absorber is increased at the expense of the component parallel to the absorber plane.

In order to study this angular distribution change as a function of absorber thickness for both front and back scattering, a point source of  $\text{Co}^{60}$  radiation was placed at the center of a very thin Formvar film mounted in a 1-in. diam hole in a thin aluminum sheet. Absorbers could be attached on either side of the radiation source, and the sheet and absorbers could be rotated with respect to the counter. Measurements were made only to  $60^\circ$  on either side of the original horizontal position to avoid possible effects of scattering by the supporting plate and absorber holders. The point source was on the axis of rotation.

As the angle was increased, the effective absorber thickness increased such that if the angle between the normal to the absorber plane and the direction of the detector was  $\theta$ , the effective thickness was  $x \sec \theta$ , where  $x$  was the sheet thickness. From the observation that when absorption measurements were made with the source and absorber close to the tube window the absorption was approximately exponential, correction for this increase in thickness was made.

Due to the fact that the active source had to be

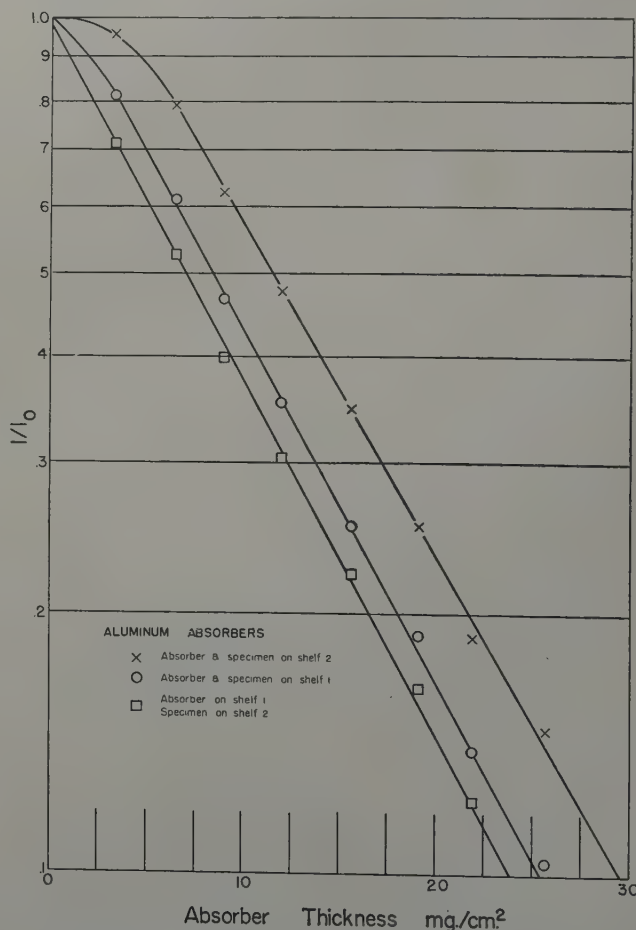


Fig. 3—Effect of counting geometry on the absorption curves obtained on diffusion disks with  $\text{Co}^{60}$  activity on the surface.

\* We were unaware at the time this paper was submitted for publication of the experimental determination of the angular distribution of absorbed  $\text{P}^{32}$  radiation performed by Yaffe and Justus (L. Yaffe and K. M. Justus: *Journal Chem. Soc., London, Supplementary Issue No. 2, 1949*). It is most interesting to have confirming evidence of his anisotropy with beta radiation from a different source. Our conclusion that back scattering is isotropic is confirmed by these authors only for thin back scatterers. Their results show an increase in anisotropy as the back scatterer becomes thicker. However, as this anisotropy is small compared to the forward scattering anisotropy, the basic argument used in our paper is still valid.



mixed with a small amount of rubber cement to fix the position on the Formvar film, there was a small and irregular variation in the distribution of the radiation. However, the results of the angular distribution measurement shown in Fig. 2 give the ratio of the activities with and without absorber for each position and this irregularity cancels out. The top curve is the result of the back-scattering measurements while the four lower curves give the results of forward scattering for increasing absorber thicknesses. The back-scattering process shows no variation in angular distribution caused by the presence of the backing absorber. The forward-scattering curves show that the effect is greatest for the thinner absorbers and becomes less as the absorber thickness is increased.

On the basis of these measurements, it is possible to understand the dependence of the absorption measurements on the counting geometry. For some solid angle comprising a cone with the axis of rotation normal to the absorber, the number of detected particles will be proportionately greater than were originally in that solid angle before the scattering process. For regions outside of this solid angle, the scattering process will cause a relative depletion in the number of particles. If the counting tube is situated at such a distance that it detects only this critical solid angle, or part of it, the relative counting rate will increase as the absorber thickness increases. However, as Fig. 2 shows that the change in angular distribution becomes less as the absorber thickness increases, the decrease in the counting rates caused by the absorption processes becomes the important factor and the absorption curve becomes more nearly characteristic of the absorption processes alone. If the specimen is located closer to the counting tube, the region detected will include an increasing amount of the loss region and the net effects of scattering are more nearly cancelled out. The optimum geometry is obviously obtained by internal sample counting. If this is impossible, the sample should be brought as close to the tube as conditions permit.

In diffusion measurements the sample itself acts as absorber and scatterer. Therefore it is necessary to measure absorption curves with the absorber as close to the sample as possible to reproduce this condition. The curves in Fig. 3 illustrate these effects. The first counting shelf was located at a distance of 0.729 cm from the tube window while the second shelf was located at a distance of 3.64 cm. The lower curve shows the effect of placing the absorber on the first shelf and the specimen on the second. The lowering of this curve is caused by the collimation of the incident beam by the aluminum shelf which supported the absorber.

### Effect of Surface Irregularities

Because of the scattering of electrons, detailed consideration of the diffusion process at the surface of the specimen is necessary. These irregularities may be due to abraiding, chemical etching, or thermal etching of the surface during the diffusion anneals. The detailed consideration for any particular case would of course depend on the exact form of the surface. However, the general situation may be visualized by consideration of a simple case which should provide the worst scattering effects. This will consist of triangular grooves of such steepness that the normals to the microsurface form angles with the normal to the macrosurface which

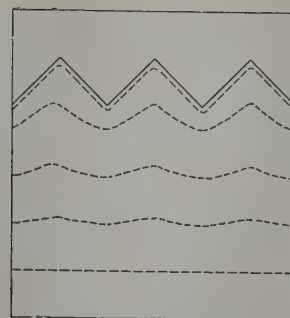


Fig. 4—Iso-concentration lines for different degrees of diffusion penetration into an irregular surface.

exceed the angle of increased activity due to scattering. Analytical solution of the diffusion equation even for this simplified case is difficult, but a qualitative consideration of the diffusion into this type of surface will suffice.

As the active atoms first diffuse into the base metal, iso-concentration lines will originally follow the microsurfaces. As diffusion progresses, the iso-concentration lines will begin to approximate the macrosurface and will become essentially parallel to it when the diffusion distances are large with respect to the surface irregularities. This sequence of events is shown schematically in Fig. 4. This, together with consideration of the scattering behavior, will permit discussion of the effects of the surface irregularities on the emitted radiation. The initial active film which is of the order of atomic dimensions will not scatter the radiation to an appreciable extent. Further, backscattering from the irregular surface will not cause a change in the angular distribution of the radiation. Therefore, the deposited layer will emit isotropically. As the active atoms diffuse into the surface, there will be a comparatively large decrease in the measured activity since the radiation will be scattered away from the detector in the direction of the normals to the microsurfaces. As diffusion progresses, the directions of maximum intensity will move from the normals of the microsurfaces in the direction of the normal to the macrosurface and will eventually coincide with it.

The correctness of this picture may be checked experimentally in at least three ways: First, by comparison of diffusion coefficients from specimens with differing surfaces. Three series of experiments were performed which may be compared by consideration of the diffusion coefficients at the same temperature, 1000°C. The first series was abraided with 4-0 emery paper; the second was etched in hot concentrated hydrochloric acid; and the third was electrolytically lapped. This is a sequence of increasing smoothness. The comparison of the apparent cobalt self-diffusion coefficients at 1000°C, calculated on the assumption of plane surfaces, is given in Table I.

It will be observed that the rougher surfaces give the higher rates of diffusion. In order to evaluate the significance of the results, it is necessary to remember that the absorption curves used in the calculation of the diffusion coefficients represent the combined effects of absorption and scattering in a plane parallel film of metal of radiation from an emitting source where the angular distribution of the radiation is isotropic. If there is any scattering of the radiation away from the normal to the macro-

surface, this will be equivalent to higher absorption in the specimen, indicating a greater depth of penetration and a higher rate of diffusion. As diffusion into polished surfaces most nearly duplicates the assumed conditions only the work done on these surfaces is presented as representing the true diffusion rates.†

The second check on the validity of the above picture is the dependence of the calculated diffusion

Table I. Cobalt Self-diffusion Coefficients at 1000°C

|                 |                                               |
|-----------------|-----------------------------------------------|
| Abraided        | $5 \times 10^{-12}$ cm <sup>2</sup> per sec   |
| Etched          | $2.4 \times 10^{-12}$ cm <sup>2</sup> per sec |
| Electropolished | $0.7 \times 10^{-12}$ cm <sup>2</sup> per sec |

Table II. Activity Measurements of a Cobalt Specimen Pair

| Time,<br>sec $\times 10^{-5}$ | Activity<br>Ratio | Apparent<br>Diffusion Coefficient<br>cm <sup>2</sup> per sec $\times 10^{12}$ |
|-------------------------------|-------------------|-------------------------------------------------------------------------------|
| 0.2688                        | 0.850             | 4.78                                                                          |
| 0.9162                        | 0.757             | 3.93                                                                          |
| 2.033                         | 0.674             | 2.94                                                                          |
| 3.823                         | 0.595             | 2.58                                                                          |

Table III. Activity Ratios and Calculated Diffusion Coefficients of Two Cobalt Specimens

| Specimen | Shelf One         |                                                                       | Shelf Two         |                                                                       |
|----------|-------------------|-----------------------------------------------------------------------|-------------------|-----------------------------------------------------------------------|
|          | Activity<br>Ratio | Diffusion<br>Coefficient,<br>cm <sup>2</sup> per sec $\times 10^{12}$ | Activity<br>Ratio | Diffusion<br>Coefficient,<br>cm <sup>2</sup> per sec $\times 10^{12}$ |
| 13       | 0.544             | 1.29                                                                  | 0.672             | 1.23                                                                  |
| 14       | 0.510             | 1.64                                                                  | 0.616             | 1.76                                                                  |
| avg.     | 0.527             | 1.45                                                                  | 0.644             | 1.48                                                                  |

coefficients on the amount of diffusion as measured by the ratio of activity of the specimens after and before diffusion for specimens with irregular surfaces. As there is an initial scattering of the radiation away from the normal to the macrosurface which becomes less as diffusion proceeds, the calculated diffusion coefficients should be high after short times and decrease as the activity ratio decreases. This conclusion was experimentally verified by interrupting the diffusion process at various times for activity measurements. Table II shows the results on a cobalt specimen pair with etched surfaces diffused for increasing times at 1000°C.

The third check is provided by comparison of diffusion coefficients calculated from activity ratios measured at different distances from the tube using

† After this manuscript was prepared a note on cobalt self-diffusion appeared: F. C. Nix and F. E. Jaumot, Jr., *Physical Review* (1950) 80, 119L. Their equation,  $D = 0.367 e^{-67000/RT}$  cm<sup>2</sup> per sec for points at 1050°, 1150°, 1250°C., corresponds to higher diffusion coefficients than those reported here, but lower than unreported values obtained on ground (4-0 emery paper) and etched surfaces. In the absence of a description of their surface preparation, no conclusions may be drawn.

absorption measurements made at those distances. Two cobalt specimens were diffused at 970°C for  $4.93 \times 10^6$  sec. The activity ratios and calculated diffusion coefficients are shown in Table III.

Although the measured activity ratios are quite different using the two geometries, the diffusion coefficients calculated using the absorption curve appropriate to each geometry show good agreement.

Much work remains to be done in order to fully understand and interpret this scattering effect. As only one radiation source was used in these experiments, the effect of such variables as particle energy is not known. However, as this method of measuring diffusion coefficients provides a more rapid and potentially more accurate technique for low diffusion rates than the conventional sectioning methods, further investigation of these scattering phenomena should be of great interest.

### Summary

The cobalt self-diffusion coefficients have been measured using the decrease in surface activity method and found to satisfy the equation:

$$D = 0.032 \exp \left( \frac{61.9 \pm 3.5}{RT} \right) \text{ cm}^2 \text{ per sec}$$

The diffusion coefficients for very dilute cobalt in nickel measured in the same way have been found to satisfy the equation:

$$D = 1.46 \exp \left( \frac{68.3 \pm 2.0}{RT} \right) \text{ cm}^2 \text{ per sec}$$

(The activation energies are in kcal per mol.)

Scattering of the beta radiation was measured and found to influence the calculated diffusion coefficients to a very significant extent.

### Acknowledgments

The authors wish to express their gratitude to the Office of Naval Research for the support of this work, to R. F. Mehl for numerous discussions during the course of these studies, and to L. F. Gronholz and J. Ferrin for much of the radioactive counting. The Co<sup>60</sup> used in these experiments was obtained from the Isotopes Division, U. S. Atomic Energy Commission.

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- <sup>5</sup> T. B. Novey and N. Elliott: *Plutonium Project Record* 9B, 2.2.2.
- <sup>6</sup> B. P. Burt: *Nucleonics* (1949) 5, No. 2, pp. 28-43.
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### Correction

In the January 1951 issue: TP 2989 D. *Industrial Hygiene in American Smelting and Refining Company* by John N. Abersold and K. W. Nelson. P. 36, Ref. 2 should read: B. R. Small, with appendix by C. A. Stevenson: *Air Conditioned Crane Cabs. Engineering Series Bulletin* 4. Industrial Hygiene Foundation of America. Mellon Institute, Pittsburgh, Pa. (1947).



# Formation and Behavior of Subboundaries in Silicon Iron Crystals

by C. G. Dunn and F. W. Daniels

IN recent publications<sup>1-5</sup> the existence and behavior of subgrain boundaries in high-purity metals has been clearly brought to light. Lacombe and Beaujard<sup>1</sup> by means of special etching methods disclosed in polycrystalline sheets of aluminum the existence of substructures differing in orientation by small amounts (about  $\frac{1}{4}^\circ$ ). Boundaries of these structures at relatively high temperatures had the remarkable property of moving about while the ordinary boundaries remained stationary. Cahn<sup>2</sup> also observed substructures in bent and annealed single crystals of aluminum, zinc, magnesium, and rock salt. The position of subboundaries could be explained in terms of a *dislocation mechanism of polygonization* in which dislocations move into lines at right angles to the bent glide planes thereby relieving elastic stresses in these planes. Guinier and Tennevin<sup>3, 4</sup> disclosed the further interesting feature that polygonized structures coarsened significantly upon prolonged annealing.

Somewhat similar subgrain phenomena have been observed in silicon iron of commercial purity. Although some evidence for the development of macro-mosaic structures in silicon iron already has been reported by one of the authors<sup>6, 7</sup> under the phenomenological term "crystal recovery," much better evidence recently has been obtained due to improved etching techniques. In addition, phenomena regarding structural changes have been uncovered.

The present investigation is divided into three parts: (1) The phenomenon of Laue spot sharpening on annealing cold-rolled crystals, (2) the phenomena of polygonization and subgrain coarsening

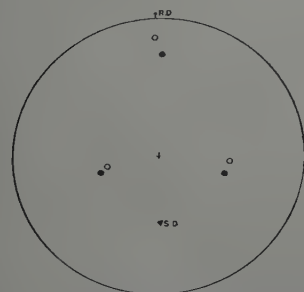


Fig. 1—Stereographic projection of {100} cube poles and the probable most active <111> slip direction. Open circles give original orientation and solid circles the orientation after cold rolling.

in (a) bent single crystals and (b) cold-rolled crystals, and (3) boundary and subboundary interactions.

## Procedure

The material used in the present investigation was high-grade commercial silicon iron sheet of nominal composition, 3.3 pct Si, 0.004 C, 0.011 P, 0.010 S, 0.04 Mn, 0.01 Al, 0.04 Cu, 0.01 Sn. Large single crystals of this material were prepared for cold-rolling or bending as scheduled. Cold-rolling of 12 pct was carried out on a laboratory 8-in. diam rolling mill. The bending deformations were performed by pressing the crystals between a solid

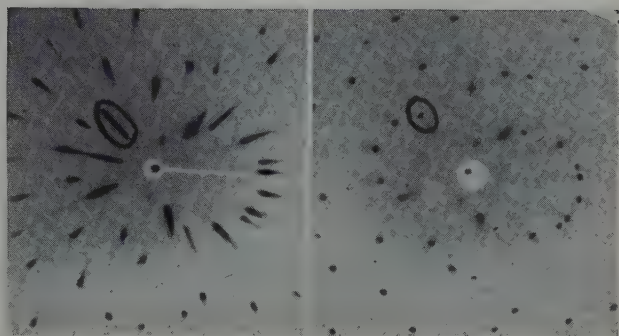


Fig. 2—Illustrative Laue patterns to show Laue spot sharpening. a (left)—Specimen as cold rolled. b (right)—After 48 hr at 1400°C.

round bar and a mating half cylinder, both heavily greased. Individual specimens were cut from the deformed crystals, and the cut edges were deeply etched prior to annealing. Laue photographs were made using 40-kv tungsten radiation. The technique used to disclose the various subboundaries was an electropolish and electroetch in a bath of chrome-acetic acid.<sup>8</sup> The anodic polishing done at 22 v was immediately followed by etching at a reduced voltage, which was dependent upon the nature of the subboundaries.

## Phenomenon of Laue Spot Sharpening on Annealing Cold-Rolled Crystals

Fig. 1 gives the initial and final orientations of the specimens cold-rolled 12 pct. Each specimen was annealed at a temperature and for a time which caused significant structural changes as evidenced by alterations in Laue patterns.

Representative Laue patterns<sup>9</sup> and micrographs showing the essential changes are given in Figs. 2, 3, and 4. The essential points to be derived from these illustrations follow:

1. Annealing at 950°C clearly develops a substructure with the orientation of the cold-rolled specimen.

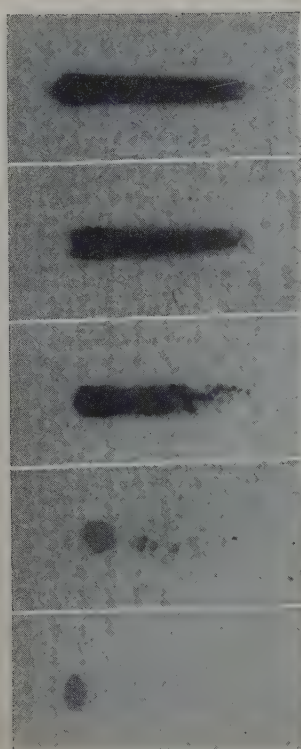
2. The subboundaries formed obviously separate regions of nearly the same orientation. Some of the subboundaries appear as a sequence of dots similar to those observed in aluminum by Lacombe and Beaujard,<sup>1</sup> but whether this is due to extremely small differences in orientation is not known at present.

3. The substructure coarsens upon prolonged annealing.

4. Prolonged annealing also causes a decrease in orientation spread according to Laue spot sharpening.

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a

b

c

d

e

Fig. 3 (left)—Enlarged Laue spot for encircled position of Fig. 2.

a—Cold rolled. b—10 min at 950°C. c—5 hr at 1000°C. d—1 hr at 1200°C. e—48 hr at 1400°C.

Fig. 4 (right)—Micrographs of cold-rolled specimens after various anneals.

Electro etch. X200. Reduced approximately 33 pct for reproduction. a (top)—10 min at 950°C, longitudinal section. b (center)—1 hr at 1200°C, longitudinal section. c (bottom)—48 hr at 1400°C, transverse section.



5. These alterations in the Laue photographs and the accompanying coarsening of the structure may be interpreted to mean that a *selective* growth of subgrains has occurred. Stated another way subgrains with orientations further removed from the average orientation of the composite are consumed by those closer in orientation to the average.

### Phenomena of Polygonization and Subgrain Coarsening

**Bent Single Crystals:** A number of bent specimens were prepared from a large single crystal 0.025 in. thick. Fig. 5 gives the pertinent crystallographic directions and the axis of bending which coincides with a  $[1\bar{2}1]$  direction. Preliminary X-ray and micrographic data for annealed specimens disclosed that high-temperature annealing produced many lamellar shaped subgrains within each original crystal. X-ray data, for example, disclosed that each Laue spot changed to a discrete set of smaller spots (a fine structure) covering the original orientation range. Fig. 6 shows such a set obtained by using an X-ray camera in a focusing position to obtain maximum sharpness of the spots. The average difference in orientation from these patterns is (a)  $0.22^\circ$  or (b)  $0.23^\circ$ . Fig. 7 shows the accompanying microstructure in a plane perpendicular to the axis of bending, see Fig. 5. The structure was disclosed by a thermal etch—a method often superior to ordinary chemical etches but far inferior to the chrome-acetic acid electroetch. One may speak of the foregoing structure as polygonized.\*

Regarding the boundary orientations, the present boundaries lie approximately  $90^\circ$  to the  $[111]$  direction as shown in Fig. 7, and this raises a question regarding possible crystallographic relationships between boundary directions and active slip planes

as predicted by the dislocation mechanism of polygonization.

To check the crystallographic relationships for formation of the new boundaries, visible traces of active slip planes were obtained before annealing and compared with the boundaries formed in a subsequent anneal. Fig. 8a shows that there are two sets of slip lines corresponding to slip on the  $(10\bar{1})$  and  $(011)$  planes. Fig. 8b shows the final subboundary for the identical area after a high-temperature anneal (subboundaries are very faint) and Fig. 8c also shows a representative structure at this point. Comparison of the photographs discloses that the boundary lines are perpendicular to the  $(10\bar{1})$  slip lines which, in this case, coincide with the  $[111]$  direction. Disregarding slip on  $(011)$  planes, the results agree well with those predicted on the basis of movement of dislocations ( $[\bar{1}21]$ -edge dislocations which are perpendicular to the plane of the microsection) until they form subgrain boundaries at  $90^\circ$  to the  $(10\bar{1})$  slip plane (this plane is in the maximum shear position and, therefore, probably the most active one during plastic bending). More will be said about this later.

\* The descriptive term *polygonized* was supplied by E. Orowan and R. W. Cahn to indicate that the line of atoms in a specific crystallographic direction taken in each subgrain along the arc of the bend forms part of a polygon. Also if the lattice is elastically bent prior to annealing, there is no polygonized state until a subdivision into unbent units occurs. This breakup into unbent units is called *polygonization*.



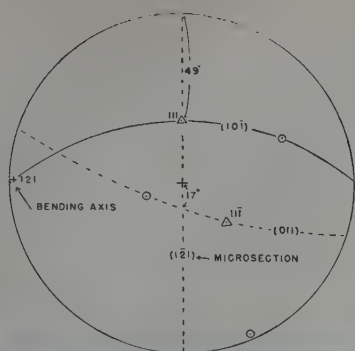


Fig. 5 (left)—Stereographic projection showing {100} poles of crystal in approximately (210) orientation, important {110} slip planes, axis of bending, and plane of the microsections.

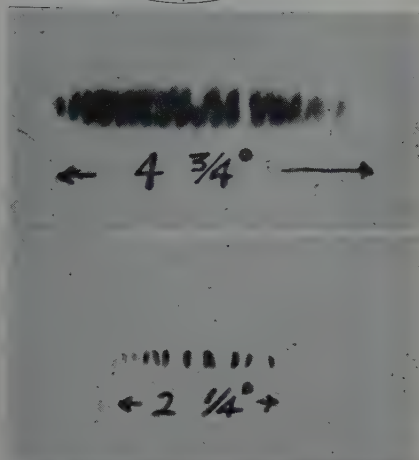


Fig. 6 (left)—Enlarged Laue spots of bent specimen P5, 3/8 in. radius, after 22 hr at 1300°C.

a (top)—0.030 in. pinhole system.  
b (bottom)—0.010 in pinhole system.



Fig. 7 (left)—Microstructure of specimen P5 after 22 hr 1300°C anneal in argon. Thermal etch. X200.

Other specimens were used to investigate the early stages of formation of the polygonized structure and also the effect of amount of bending. Three parts (P2, P3, and P4) of the original crystal were bent to radii of 21/32, 3/8, and 3/32 in., respectively. Each part was further divided into a number of specimens for various treatments. Fig. 9 shows the microstructure of some P3 specimens before and after heat treatment, the latter three being a sequence on a single specimen. Another P3 specimen of importance but not photographed was annealed 15 min at 775°C.

The micrographs disclose a coarsening of the substructure as well as the formation of subboundaries 90° to the direction of (101) slip lines. The slip lines here are revealed after sectioning and therefore are representative of interior regions of the bent crystal. These lines are not called subboundaries. The subboundaries initially formed are very wavy and often appear to terminate in the matrix; only later in the annealing do they become relatively straight. Some areas in the 775°C annealed specimen disclosed no subboundaries, other areas did. Among these subboundaries there were some that

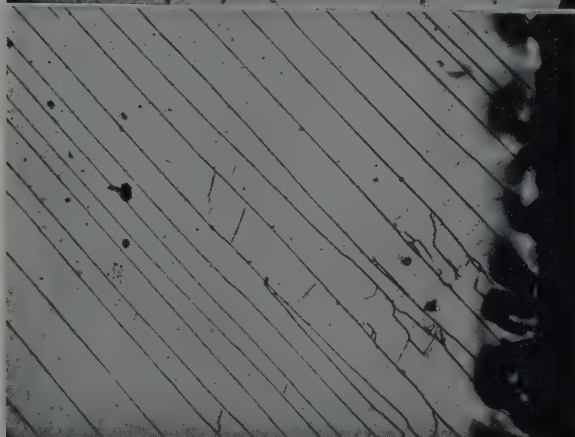
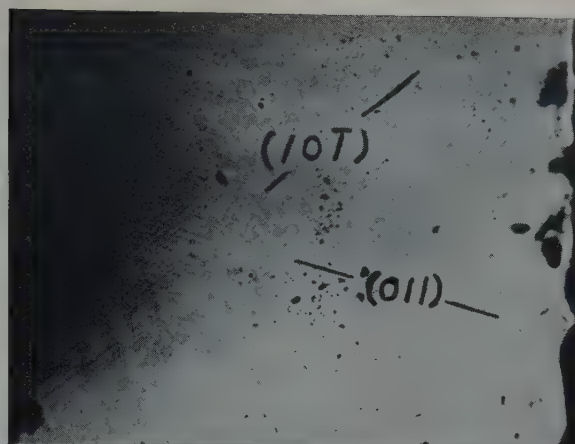


Fig. 8 (above)—Microstructure of bent specimen P1, 21/32 in. radius, before and after annealing.

X150. Reduced approximately 33 pct for reproduction. a (top)—Polished then bent. b (center)—After 1 hr at 1300°C in argon. Same area as a. Thermal etch. c (bottom)—Representative structure. Electro etch.

extended only from one slip line to another.

Figs. 10 and 11 show micrographs for the P2 and P4 series, respectively. P2 appears incompletely transformed after 10 min at 950°C. Lines that coincide with the original slip lines are still present and the structure in general is quite heterogeneous. The increase in subgrain size on prolonged annealing at 950°C is very striking. Specimen P4 reacted to the 950°C anneals in somewhat similar fashion, the coarsening, however, being less pronounced. The 1300°C treatment converted P4 to a single crystal of new orientation. Unlike the subgrains, which had a common [121] direction, this new crystal had a different orientation and therefore could not have been one of the observed subgrains which had grown at the expense of others. The origin of this grain is beyond the scope of the present paper; it

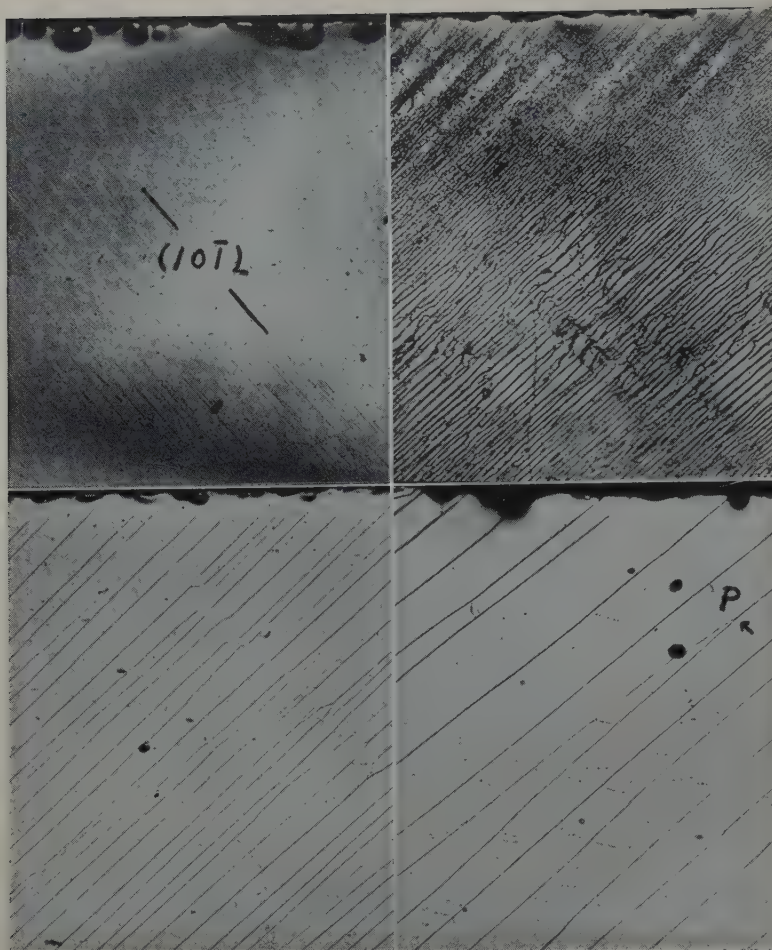


Fig. 9—Microstructure of bent specimen P3, 3/8 in. radius, before and after various anneals.

Electro etch. X200. Reduced approximately 33 pct for reproduction. *a* (upper left)—Bent and sectioned to show slip lines. *b* (upper right)—After 10 min at 950°C. *c* (lower left)—After 24 hr at 950°C. *d* (lower right)—After 4 hr at 1300°C.

is more properly dealt with under the phenomenon of primary recrystallization.

X-ray data representing early and late stages of the treatments are shown in Figs. 12 to 14. Annealing for 10 min at 950°C appears to have produced a change in the uniformity of the Laue spot for specimen P3. No such change, however, is apparent for P2, and a nonuniform Laue spot for specimen P4 is present both before and after annealing. It might be concluded from these X-ray data that specimen P4 was partly polygonized before annealing, that specimen P3 polygonized some in the 10-min 950°C anneal, and that P2 did not polygonize at all in the same anneal. However, the micrographic data indicate degrees of polygonization not resolvable by the present X-ray technique. No refined technique such as that employed by Guinier<sup>8</sup> was attempted, however, since the micrographs were entirely satisfactory for revealing early structures. After appreciable subgrain coarsening, ordinary X-ray techniques sufficed to determine the nature of the substructure.

Table I. Average Width of Subgrains in Microns

| Anneal         | P2   | P3   | P4  | P5   |
|----------------|------|------|-----|------|
| 10 min at 950° | 3.5  | 5.1  | 2.2 |      |
| 24 hr at 950°  | 18.3 | 13.7 | 3.7 |      |
| 4 hr at 1300°  | 42.5 | 35.3 |     |      |
| 22 hr at 1300° |      |      |     | 39.5 |

Table II. Angle of Separation  $\theta$  in Degrees

| Anneal         | P2    | P3    | P4    | P5   |
|----------------|-------|-------|-------|------|
| 10 min at 950° | 0.017 | 0.043 | 0.075 |      |
| 24 hr at 950°  | 0.088 | 0.12  | 0.13  |      |
| 4 hr at 1300°  | 0.21  | 0.30  |       | 0.19 |

The widths of lamellar subgrains were measured to obtain the values given in Table I.

Using an angle of 45° for the directions of the boundaries and assuming a progressive rotation of the subgrains, geometry considerations indicate that the average angle between adjacent lamellae should be, to a good approximation:

$$\theta = \frac{W \times 57.3}{R (0.707)} \quad [1]$$

where  $W$  is the average width of the subgrains and  $R$  is the radius of bend. With this equation and the foregoing data the values given in Table II were obtained.

The largest subgrains were approximately double the average size. The values of 0.19° for specimen P5 and 0.21° for P2 obtained from eq 1 agree well with the X-ray diffraction value of 0.22° or 0.23° given previously for specimen P5. This agreement justifies the assumption of a progressive rotation of the subgrains *after coarsening*. On the other hand it does not prove that the *initial subgrains* actually differed in orientation by 1' to 4' (0.02° to 0.07°) as calculated in Table II.

**Cold-rolled Crystals:** In Fig. 4a, there are narrow lamellae in certain regions of the microstructure, which look very similar to the lamellae developed in bent specimens. The crystallographic relationship obtained from Figs. 1 and 4a show that the parallel boundary lines are approximately 90° to a  $\langle 111 \rangle$  direction, S.D., which should have been active according to the orientation change produced during deformation. This part of the transformation, therefore, appears to be identical with that occurring in bent specimens and suggests that local regions of the lattice were bent during cold-rolling.



The structure in such local regions after annealing, therefore, may be described as polygonized. As the structure coarsens, however, it has less and less the characteristics of a polygonized one, not because the lamellar structures vanish but because larger units no longer have simple relationships in an orientation sequence. The coarsened structure is probably better described as macromosaic. At the stage of coarsening represented by Figs. 3d and 4b, however, there still are present a number of parallel boundaries in the direction of the original polygonized lines and this indicates some persistence of the structure. A similar situation appears to have been the case in an example of crystal recovery cited by Dunn<sup>7</sup> (see his Figs. 8, 9, and 10), because if  $\langle 111 \rangle$  directions are added to Fig. 10, they fall roughly  $90^\circ$  to the subboundaries of the micrograph.

### Boundary and Subboundary Interactions

The results of boundary and subboundary interactions reported in this section are largely of a preliminary and qualitative nature.

The simplest example of interaction involves two grains, one in a strain free state, the other containing considerable substructure as shown in Fig. 15, for example. As in the case of specimen P4 described previously, grain A is the result of primary recrystallization but, in this example, has not completely consumed the polygonized grain. Although primary recrystallization may provide suitable examples of interaction as illustrated above, greater control of the variables is possible if two-grain specimens are made in another way.

In the controlled method one grain is grown until about half of a fine-grained specimen is transformed. The entire specimen is then bent and the untransformed area is converted to a second grain. In this second step the first grain undergoes polygonization. A Laue photograph, such as Fig. 16a taken at the grain boundary of a completed specimen, would show one grain in the strained condition and the other strain free as evidenced by Laue asterism and sharp Laue spots, respectively. Micrographs of such specimens, however, show that the strained grains actually are polygonized.

When a specimen is annealed at temperatures of  $1200^\circ$  to  $1300^\circ\text{C}$ , the strain free grain grows at the expense of the polygonized grain, with parts of the boundary often moving away from their centers of curvature. In other words the situation appears to be similar to that of growth into a strained matrix. Since the surface tensions of the subboundaries no doubt are small, one should expect near  $180^\circ$  grain boundary angles at boundary and subboundary junctions and consequently little evidence for subboundary driving energy from the geometry of the boundary, see Fig. 15. Nevertheless, the major driving energy in the present illustrations reasonably resides at the subboundaries. The ideas of Bragg,<sup>9</sup> Burgers,<sup>10</sup> and Smith<sup>11</sup> on subboundaries and subboundary energies are particularly pertinent to this view although some of the ideas apply more specifically to the cold-worked state.

A more complicated type of interaction involves two grains each with subboundaries. For example, a two-grain specimen may be cold rolled and annealed with each part behaving as in the early illustration—that is, developing substructures, which coarsen while the subboundaries apparently balance out at the boundary. Such coarsening of a substructure was of course not observed in previously pub-

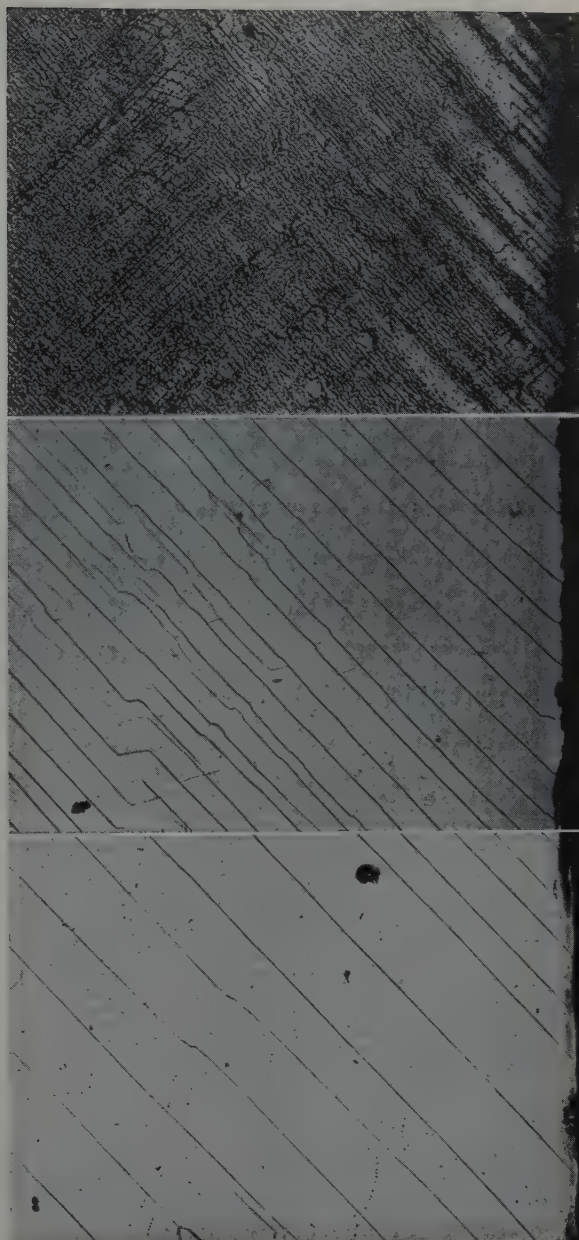


Fig. 10—Microstructure of bent specimens P2, 21/32 in. radius, after various anneals.

Electro etch. X200. Reduced approximately 33 pct for reproduction. a (top)—After 10 min at  $950^\circ\text{C}$ . b (center)—After 24 hr at  $950^\circ\text{C}$ . c (bottom)—After 4 hr at  $1300^\circ\text{C}$ .

lished work on silicon iron<sup>6,7</sup> where the ordinary boundaries remained essentially unchanged during Laue spot sharpening. However, since the conditions of deformation and annealing were similar to those of the present work, it is believed that subgrain coarsening did occur and was responsible for the observed sharpening of Laue spots.

Some cases have been observed in cold-rolled specimens where one grain grows at the expense of the other (a case of unbalanced subboundaries). Examination of the area swept by the grain boundary usually discloses the presence of subboundaries, which continue back to the original position of the boundary. This means that subboundaries are "pulled along" with the boundary as it moves. Some of the subboundaries produced in this way separate regions differing in orientation by a degree or two. The appearance of grain boundaries in the strain-induced grain boundary migration experiments in high-purity aluminum of Beck and Sperry<sup>12</sup> indicate that subboundaries no doubt would be formed



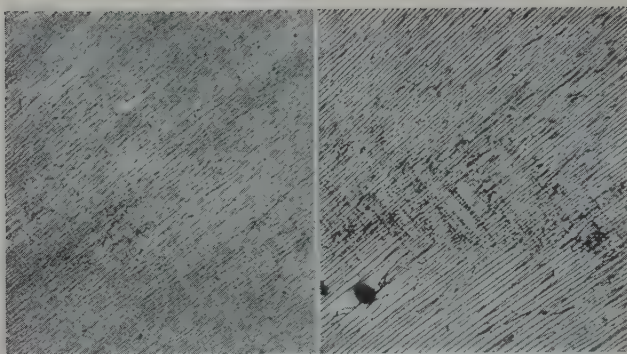


Fig. 11—Microstructure of bent specimens P4, 3/32 in. radius, after various anneals. Electro etch. X200. a (left)—After 10 min at 950°C. b (right)—After 24 hr at 950°C.

similarly in the traversed areas. It is, therefore, not very surprising that the strain-anneal method for producing large crystals in high-purity aluminum often produces rather imperfect crystals as reported by Lacombe.<sup>18</sup>

That an unbalance of subboundaries adjacent to an ordinary boundary will promote migration of the latter can readily be shown. To illustrate, if the specimen of Fig. 16a is again bent and polygonized (see Fig. 16b), the resulting two grains differ in their subboundary energy per unit volume and the one that is least bent (lowest energy in this case) will grow at the expense of the other. In a 1300°C, 3-hr anneal the boundary for this case actually moved a small amount. X-ray and micrographic data disclosed that the subboundaries moved along with the grain boundary, altering but not removing polygonization in the traversed area. The polygonized state in the area traversed by the boundary clearly did not originate through a *dislocation-mechanism of polygonization* as described by Cahn; rather it arose from growth of a polygonized region adjacent to it. Since this phenomenon may occur under less controlled conditions, it follows that simple growth processes may play a role in the development of polygonized areas. Alterations in the substructure and thus alterations in the detailed picture of a polygonized state through growth of the subgrains have, of course, already been discussed.

### Energetics of Boundary and Subboundary Migration

**Boundary Migration:** The grain boundary energy equation of Shockley and Read<sup>14</sup> should apply especially well to subboundaries, because the orientation differences involved are very small. The equation is:

$$E = E_0 \theta (A - \ln \theta) \quad [2]$$

where  $E$  is the energy per unit area of grain boundary,  $\theta$  is the difference in crystal orientation, and  $E_0$  and  $A$  are approximately constants.

Assuming eq 2 applies and that the energy reaches a maximum at  $\theta$  equal to 30°, it follows that the energy in a subboundary of coarsend substructure ( $\theta$  equal to 0.2°) is about 1/25 the maximum value (i.e., approximately 1/25 that of an ordinary boundary). With smaller  $\theta$ 's the energy would be less than this.

The energy per unit volume, or the driving force, is more important for boundary migration. Assuming a uniform lamellar substructure of width  $w$  equal to  $40\mu$  and a  $\theta$  value of 0.2°, it follows that the energy per unit volume would be:

$$\frac{E(0.2^\circ)}{w} = \frac{E_{30}}{25w} = 10E_{30} \quad [3]$$

This value of available driving force is approximately the same as that obtained in grain-growth experiments on two-grain specimens of silicon iron carried out at temperatures of 1300° to 1400°C and appears to be near a lower limit for ordinary grain-boundary migration at these temperatures.<sup>15</sup> An estimate of the absolute value of this energy per unit volume indicates that it would be about  $10^{-6}$  that measured for heavily cold worked iron.<sup>†</sup>

Growth of a grain at the expense of another because of subboundary energy in one of them, as was illustrated in Fig. 15, would be expected to be slow, therefore, according to these estimates of available driving force.

A more general energy relationship for lamellar subgrains can be written in terms of the orientation difference  $\theta$  and the radius of bend  $R$ , since these quantities together with the boundary direction  $\phi$  determine the width of the subgrains. From eqs 1 and 2 it follows that:

$$\text{Energy per unit volume} = \frac{E_0 (A - \ln \theta)}{R \cos \phi} \quad [4]$$

where  $\phi$  generally is near 45°.

According to this equation the average driving force for boundary migration decreases with increasing values of  $\theta$  and  $R$  indicating: (1) That subgrain coarsening lowers the total energy as it should and (2) with constant  $\theta$ , less bending of the lattice leads to less energy, which also is reasonable.

When boundary migration involves subboundaries on both sides of the boundary, the driving force is

<sup>†</sup> Perhaps significant in this connection is some unpublished work on microhardness vs. crystal recovery in silicon iron crystals which has shown almost 100 pct removal of work hardening for equivalent anneals to those producing polygonization in the present investigation.

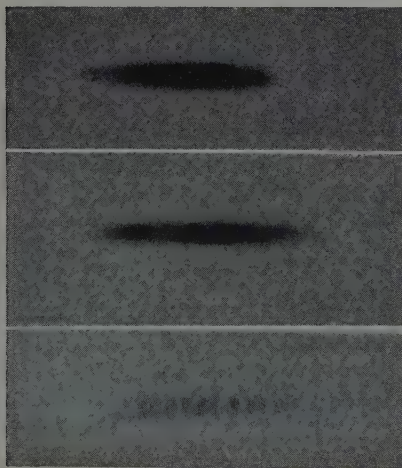
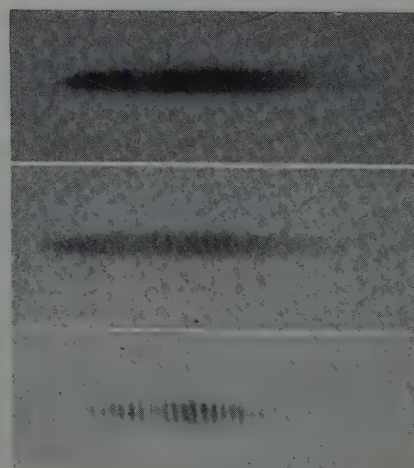


Fig. 12 (left)—Enlarged Laue spot of specimen P2.

a (top)—As-bent. b (center)—After 10 min at 950°C. c (bottom)—After 4 hr at 1300°C.

Fig. 13 (right)—Enlarged Laue spot of specimen P3.

a (top)—As-bent. b (center)—After 10 min at 950°C. c (bottom)—After 4 hr at 1300°C.





obtained as a difference in subboundary energy per unit volume. If this difference is zero, there is no net driving force to move the grain boundary. Instances may occur where the difference is so small that little movement of ordinary boundaries could be expected. This may account, therefore, for stationary grain boundaries<sup>1</sup> as well as the phenomenon of growth retardation through straining.<sup>10</sup> On the other hand, it is well known that grains in a deformed polycrystalline specimen have different degrees of straining, and this leads to the belief that many situations of unbalanced subboundaries could arise. It is suggested that strain-induced grain-boundary migration, reported by Beck and Sperry,<sup>12</sup> probably is this phenomenon.

**Subboundary Migration and Subgrain Coarsening:** Coarsening may be considered apart from any mechanism for release of subboundary energy. According to eq 4 the average energy per unit volume for a uniform substructure decreases logarithmically with  $\theta$ . This means that the available driving force for doubling the subgrain size is constant regardless of the initial size. If half the volume transforms to produce doubling, we have

$$\text{Driving force} = \frac{2E_s \ln 2}{R \cos \phi} \quad [5]$$

and this is somewhat less (a factor of 0.23) than the residual energy per unit volume for  $\theta$  equal to  $0.2^\circ$ .

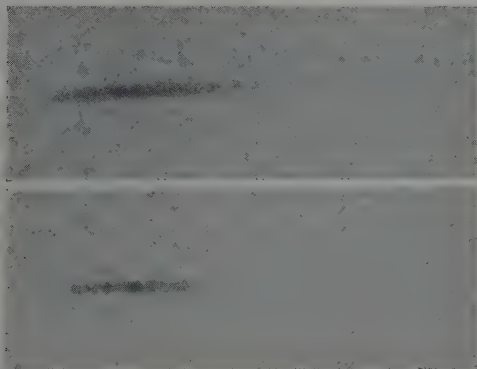


Fig. 14—Enlarged Laue spot of specimen P4. a (upper)—As-bent. b (lower)—After 10 min at  $950^\circ\text{C}$ .

Theoretically two thirds of the volume could transform with  $\theta$  increasing to  $3\theta$  due to the coalescence of three boundaries with a

$$\text{Driving force} = \frac{3E_s \ln 3}{2R \cos \phi} \quad [6]$$

and this is about 0.27 times the  $0.2^\circ$ —residual. The coalescence of three subboundaries to form one, therefore, provides slightly more driving force than the coalescence of two, but the driving force is of course not large for either case.

The probability of one lamella growing at the expense of others as in exaggerated grain growth, for example, should be low in spite of an even more favorable driving force. At the start any one lamella is not favored to grow because the driving force is

$$\frac{2E_s \ln 2}{R \cos \phi} \text{ for each. After one lamella has doubled,}$$

however, the driving energy for its further growth is greater, because coalescence of a  $2\theta$ -boundary and a  $\theta$ -boundary releases more energy for the same volume change than the coalescence of two  $\theta$ -boundaries. The situation then improves with growth but not in a rapid manner; consequently other lamellae probably would grow also before one could become particularly large.

It must be remarked here that growth of a new

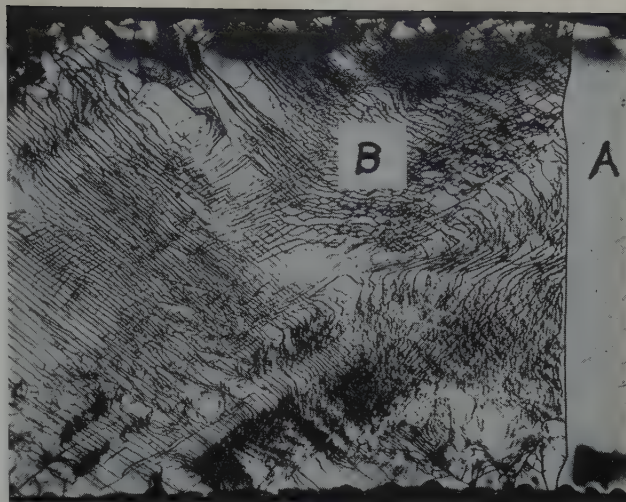


Fig. 15—Micrograph showing boundary and subboundaries of two grains A and B, with grain B in a complex polygonized state, after 4 hr at  $1300^\circ\text{C}$ .

Electro etch. X150. Reduced approximately 33 pct for reproduction.

grain at the expense of a polygonized grain (treated previously) does not have a constant driving force if growth alters the type of boundary enough to increase or decrease its specific energy.

If the driving energy is roughly constant for each stage of doubling as the above analysis would indicate, it is not at all clear why the coarsening should slow down at high temperatures. However, there must be a mechanism for the release of energy. We believe it is one of subboundary interaction quite analogous to that for ordinary grain growth. With increased annealing the reduction in number of interaction points such as that at P in Fig. 9d seems significant; interactions could move such points to the surface and thus coarsen the structure. When all have been used, coarsening should stop. On the other hand if sidewise movement of the subboundaries should occur because of unusual mobility (this is not a mechanism), some subboundaries occasionally would disappear during coarsening. Others should define very narrow lamellae just prior to disappearance, but the microstructures gave no strong evidence of this kind.

When parallel subboundaries are very close together, as they may be during polygonization, a force of attraction may exist between them, which would tend to make them coalesce. According to eq 2 if two like boundaries coalesce with one lamella going to zero width, the energy for the final subboundary will be less than that of the sum of the two initial subboundaries; so coalescence will reduce

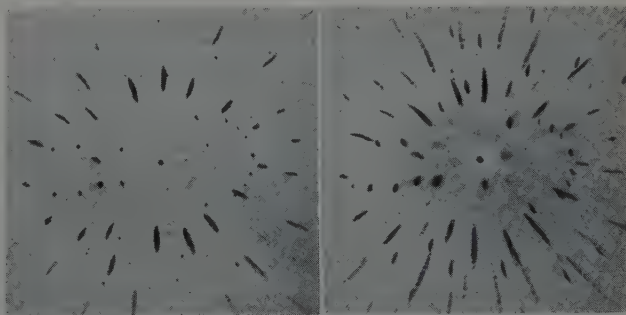


Fig. 16—Laue photograph of boundary position in a two-grain specimen.

a (left)—As-prepared. Lattice of one grain strain free, lattice of other strained to  $21/32$  in. radius bend. b (right)—After additional bending and a 3-hr anneal at  $1300^\circ\text{C}$ .



the energy. Now if it is assumed that the change in energy occurs continuously, it follows that the force of attraction is the rate of energy variation with distance of separation. Somewhat larger forces of attraction reasonably could occur for polygonized cold-rolled crystals because adjacent boundaries could consist of dislocations of opposite signs whereas boundary dislocations in a bent sample are only of one kind.

The observed coarsening of subgrains in cold-rolled crystals may be likened to normal grain growth, except for the addition of a selective growth feature. Selective growth with removal of the orientation spread, of course, leads to a lower final energy state (because energy increases with difference in orientation) and should be favored therefore on a probability basis. On the other hand the selective growth may also involve subgrain sizes, smaller subgrains having orientations farthest from the average.

Although the removal of subboundary interaction points seems to account for the slowing down of coarsening in polygonized samples at high temperatures, the amount of movement of subboundaries at low temperatures, note Figs. 10a and 10b, suggest that some feature of the kinetics besides simple interaction and energy per unit volume may be involved. In a simple polygonization process the first lamellae formed have much smaller differences in orientation than those formed later as a result of coarsening. It would appear that a small difference in orientation favors subboundary movements. Generally, however, grain-boundary migration is favored by an appreciable difference in orientation. These somewhat contradictory facts can be reconciled if it is assumed that ease of boundary migration decreases at first with difference in orientation  $\theta$ , reaches a minimum value for a relatively small value of  $\theta$  (possibly about one degree) and then increases again.<sup>†</sup> According to dislocation theory, mobility should be high for very small values of orientation difference, but theory apparently has not advanced far enough to completely explain the role of orientation relationships. For that matter much remains to be done experimentally on the same problem.

### Summary

Single crystals of silicon iron were plastically deformed either by cold-rolling or by bending and were subsequently annealed. Results of a micrographic and X-ray investigation disclosed the following:

1. The phenomenon of removal of asterisms in Laue spots of cold-rolled single crystals without recrystallization results from two processes: (a) Polygonization, which produces a relatively fine subgrain structure and (b) subgrain growth of a fairly uniform kind like normal grain growth but selective in nature, removing the major spread in orientation and thereby producing a more nearly perfect single crystal of low subboundary energy.

2. Polygonization occurs in bent single crystals with subboundaries 90° to the active slip plane. As first formed the subboundaries are far from continuous and straight. With continued annealing irregularities disappear concurrently with coarsening of the lamellar substructure, which in one instance went as far as a ten-fold increase in lamellar

width. Theoretical considerations of the kinetics involved indicate a relatively small driving energy for coarsening.

Two-grain specimens were prepared in which either one or both of the grains contained subgrains. Annealing at high temperatures disclosed the following:

1. When one grain alone contains subboundaries, the other grain grows quite readily, apparently through interaction of the subboundaries with the ordinary boundary.

2. When both grains contain subboundaries, the ordinary boundary sometimes fails to move, apparently from lack of driving energy. At the same time, however, the subgrains grow larger. At other times the boundary does move, but in general the area swept is not free of subboundaries. Subboundaries are "pulled along," so to speak, since the ordinary boundary actually separates two sets of subgrains instead of two perfect crystal lattices. The available driving energy for the movement is the difference in subboundary energy per unit volume.

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<sup>†</sup> This view of the effect of orientation difference on rate of growth was developed in a discussion of growth phenomena with David Turnbull.



# Interface and Marker Movements in Diffusion In Solid Solutions of Metals

by Luiz C. Correa da Silva and Robert F. Mehl

An experimental study of the movement of markers in the systems Cu/ $\alpha$ -brass, Cu/Sn $\alpha$ -solid solution, Cu/Al $\alpha$ -solid solution, Cu/Ni, Cu/Au, Ag/Au, employing many types of markers and a variety of temperatures. Marker movement is confirmed and undoubtedly associated with the manner in which atoms move during diffusion.

SEVERAL years ago Smigelskas and Kirkendall<sup>1</sup> reported measurements on the interdiffusion of copper and  $\alpha$ -brass and on the movement of inert markers placed at the original join. These markers were observed to move toward the  $\alpha$ -brass side of the join, and from this it was inferred that zinc diffuses in  $\alpha$ -brass more rapidly than copper. Similar results were reported a little earlier for the diffusion of solvents into high polymer solids.<sup>2</sup> This has attracted much attention, particularly from those interested in the mechanism and the theory of diffusion: Seitz<sup>3</sup> has employed it in supporting the vacancy theory of diffusion; from the data Darken<sup>4</sup> has calculated separate diffusion coefficients for copper and zinc, developing a "phenomenological" theory of diffusion; and Bardeen<sup>5</sup> has employed it in constructing a general theory, including therein the work of Seitz and Darken, as has Le Claire.<sup>6</sup> These matters have recently been reconsidered in a symposium.<sup>7</sup>

Some reason has existed for questioning the work of Smigelskas and Kirkendall.<sup>1</sup> Their technique consisted in electroplating copper on  $\alpha$ -brass, upon the surface of which Mo-wires had been secured,

and then diffusing, measuring the extent of diffusion along the normal to the join, and measuring the marker displacement in the same direction by a comparator determination of the distance between Mo-wires on opposite sides of the electroplated brass sample. It has been suspected that the copper plate might have been porous, and that the original interface might have been an imperfect join, both contributing to the transfer of the volatile zinc by vapor transfer;<sup>8</sup> it has also been questioned whether the marker movement might not in a measure be a property of the marker itself; etc. These legitimate questions require experimental answers; the present paper offers such answers.

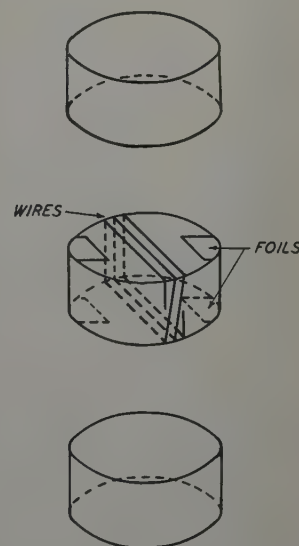
Moreover, Smigelskas and Kirkendall studied the effect only in the Cu-Zn system and at one temperature; the attention which the work of Smigelskas and Kirkendall has commanded recommends similar

Table I. Diffusion Couples

| Designation                            | Nominal Composition in Specimen (W/o) | Total Time of Diffusion, hr | Temp of Diffusion, °C | Atmosphere Used                |
|----------------------------------------|---------------------------------------|-----------------------------|-----------------------|--------------------------------|
| <b>Cu-Zn System</b>                    |                                       |                             |                       |                                |
| B 20                                   | Cu/70Cu,30Zn/Cu                       | 119                         | 880                   | H <sub>2</sub> ,N <sub>2</sub> |
| B 35                                   | 70Cu,30Zn/Cu/70Cu,30Zn                | 691                         | 784                   | N <sub>2</sub>                 |
| B 36                                   | 70Cu,30Zn/Cu/70Cu,30Zn                | 507                         | 834                   | H <sub>2</sub> ,N <sub>2</sub> |
| B 37                                   | 70Cu,30Zn/Cu/70Cu,30Zn                | 197                         | 885                   | N <sub>2</sub>                 |
| B 42*                                  | 70Cu,30Zn/Cu/70Cu,30Zn                | 533                         | 784                   | N <sub>2</sub>                 |
| B 45*                                  | 70Cu,30Zn/Cu/70Cu,30Zn                | 185                         | 883                   | N <sub>2</sub>                 |
| C 1*                                   | Cu/70Cu,30Zn/Cu                       | 257                         | 882                   | N <sub>2</sub>                 |
| C 3*                                   | Cu/70Cu,30Zn/Cu                       | 267                         | 883                   | N <sub>2</sub>                 |
| C 11*                                  | 70Cu,30Zn/Cu/70Cu,30Zn                | 85                          | 882                   | N <sub>2</sub>                 |
| C 14*                                  | Cu/70Cu,30Zn/Cu                       | 112                         | 884                   | N <sub>2</sub>                 |
| C 17                                   | Cu/80Cu,20Zn/Cu                       | 66                          | 923                   | N <sub>2</sub>                 |
| C 19*                                  | Cu/70Cu,30Zn                          | 73                          | 884                   | N <sub>2</sub>                 |
| C 20*                                  | Cu/70Cu,30Zn/Cu                       | 27                          | 884                   | N <sub>2</sub>                 |
| E 1                                    | Cu/70Cu,30Zn/Cu                       | 46                          | 884                   | N <sub>2</sub>                 |
| C 22                                   | 52Cu,48Zn/81Cu,19Zn/52Cu,48Zn         | 18 hr 50 min                | 733                   | N <sub>2</sub>                 |
| <b>Cu-Al System</b>                    |                                       |                             |                       |                                |
| B 22                                   | Cu/93Cu,7Al/Cu                        | 165                         | 977                   | He                             |
| B 34                                   | Cu/93Cu,7Al/Cu                        | 608                         | 948                   | Vacuum                         |
| B 39                                   | Cu/93Cu,7Al/Cu                        | 305                         | 889                   | N <sub>2</sub>                 |
| C 6*                                   | Cu/93Cu,7Al/Cu                        | 186                         | 994                   | N <sub>2</sub>                 |
| <b>Cu-Sn System</b>                    |                                       |                             |                       |                                |
| B 23                                   | Cu/90Cu,10Sn/Cu                       | 224                         | 804                   | N <sub>2</sub>                 |
| B 28*                                  | Cu/90Cu,10Sn/Cu                       | 164                         | 812                   | Ar                             |
| B 33                                   | Cu/90Cu,10Sn/Cu                       | 524                         | 808                   | N <sub>2</sub>                 |
| B 41*                                  | Cu/90Cu,10Sn/Cu                       | 695                         | 733                   | N <sub>2</sub>                 |
| B 46                                   | Cu/90Cu,10Sn/Cu                       | 504                         | 733                   | N <sub>2</sub>                 |
| <b>Cu-Ni, Ag-Au, and Cu-Au Systems</b> |                                       |                             |                       |                                |
| B 38                                   | Cu/Ni                                 | 362                         | 947                   | Vacuum                         |
| C 4                                    | Cu/Ni/Cu                              | 312                         | 1054                  | N <sub>2</sub>                 |
| C 21*                                  | Cu/Au/Cu                              | 92                          | 839                   | N <sub>2</sub>                 |
| D 2*                                   | Ag/Au/Ag                              | 96                          | 910                   | Ar                             |
| D 3*                                   | Ag/Au/Ag                              | 50                          | 925                   | Vacuum                         |

\* Not analyzed.

Fig. 1—Arrangement of markers of wire and foil in a (double) diffusion couple to be welded.



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Table II. Compositions of the Copper Alloys

| Nominal | Cu    | Pb    | Fe    | Ni     | Sn    | Al     | Si     | Mn    | Zn    |
|---------|-------|-------|-------|--------|-------|--------|--------|-------|-------|
| 70/30Zn | 68.92 | <0.01 | 0.025 | 0.014  | 0.039 |        |        |       | Rem.  |
| 90/10Sn | 89.82 | 0.009 | 0.004 | <0.001 | Rem.  | <0.001 | <0.002 | 0.005 | <0.01 |
| 93/7Al  | 92.65 | 0.002 | 0.030 | <0.005 |       | Rem.   | <0.002 | 0.002 | <0.01 |

OFHC copper and zinc of 99.99 pct Zn; it was melted in a graphite crucible under borax in an induction furnace. The 20 pct Zn alloy was cold-rolled 50 pct and annealed; this alloy appears in the couple C-17 (Table I). The copper was in the form of cylinders 3 in. in diam; the nickel was high-purity Mond nickel, received as disks 1 in. in diam and  $\frac{1}{4}$  in. thick.

Disks were cut to a diameter of  $1\frac{1}{4}$  in. (except in the case of Ni, left at 1 in.) and to thicknesses of  $\frac{1}{4}$  in. (for the Cu/Ni couples) or  $\frac{1}{2}$  in. (for all others). For the purposes of the experiments, the opposite faces had to be as nearly parallel as possible; with care this was done to  $\pm 0.0005$  cm; after machining the disks were polished carefully, usually with a finish from 4/0 emery paper. The surfaces were cleaned, degreased, and lightly etched with  $\text{HNO}_3$ .

The interface join markers employed were, variously:

- Type a. Molybdenum wire, 0.0075 cm diam.
- Type b. Tungsten wire, 0.0050 cm diam.
- Type c. Tungsten wire, 0.0010 cm diam.
- Type d. Platinum wire, 0.0075 cm diam.
- Type e. Platinum wire, 0.0025 cm diam.
- Type f. Platinum wire, silver coated, 0.0005 cm diam.
- Type g. Nickel wire, 0.0075 cm diam.
- Type h. Iron foil, 0.0025 cm thickness.
- Type i. Tantalum foil, 0.0025 cm thickness.
- Type j. Platinum foil, 0.0050 cm thickness.
- Type k. Nickel foil, 0.0075 cm thickness.
- Type l. Carbonaceous "wire"—made by carbonizing silk thread in vacuum.
- Type m.  $\text{Al}_2\text{O}_3$  powder (of polishing grade).
- Type n. Iron oxide "wire"—made by oxidizing a fine iron wire.

### Welding

The pressure applied for welding was the minimum possible for successful welding, usually in the neighborhood of 100 lb. The welding time was usually about 1 hr.

The specimens used usually consisted of three disks, the two outer disks identical, assembled as shown in Fig. 1. The markers in wire form were wound around the middle disk, as shown; this figure also shows the placing of foils. The composite of three disks were initially compressed hydraulically to 5000 to 15,000 lb to set the markers; this prepressing made subsequent welding much easier. After placing the disk composite in the furnace, the furnace was evacuated, then filled with hydrogen, the operation repeated several times at room temperature, and finally repeated several times while heating the furnace to  $600^\circ\text{C}$ ; the latter operation was omitted in the case of the brasses, owing to the risk of dezincing. In the case of the Cu-Al samples, special care was taken to remove all traces of oxygen (since hydrogen will not reduce  $\text{Al}_2\text{O}_3$ )—some Mg dust was employed as a getter. The time of welding was 1 hr or longer.

The metal disks were welded in the furnace sketched in Fig. 2. Heating was provided by resist-

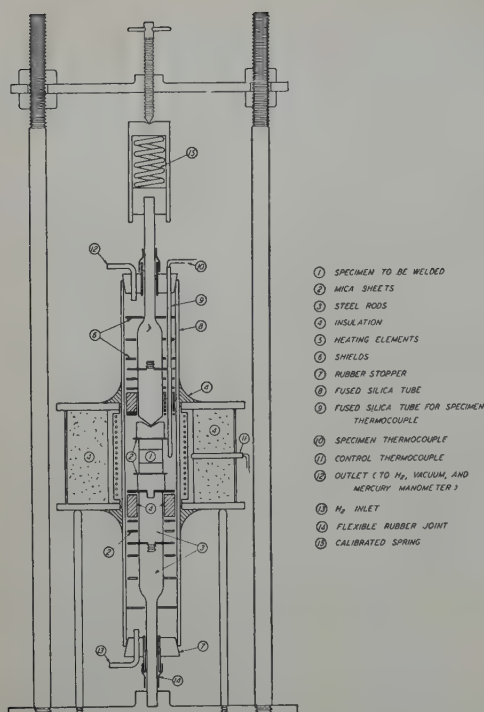


Fig. 2—  
Welding  
apparatus.

studies on other systems over a range of temperatures; the present paper offers similar studies upon six alloy systems. Diffusion couples in the following systems have been studied: (1) Cu/ $\alpha$ -brass, 30 pct Zn and 20 pct Zn; (2) Cu/Cu-Al,  $\alpha$ -solid solution, 7 pct Al; (3) Cu/Cu-Sn,  $\alpha$ -solid solution, 10 pct Sn; (4) Cu/Ni; (5) Cu/Au; (6) Ag/Au. The diffusion couples were welded disks, and of the 29 couples all were double couples ("sandwiches"), e.g., Cu/Ni/Cu, except two. Table I lists the couples employed; it also gives times and temperatures of diffusion and the protective atmosphere employed.

### Materials

Most of the alloys were prepared through the courtesy of D. K. Crampton, of the Chase Brass and Copper Co. The analyses are listed in Table II. The 30 pct Zn alloy was received in the form of rolled slab, 1 in. thick; the Cu-Sn alloy was a forged flat bar  $\frac{1}{2}$  in. thick; and the Cu-Al alloy was a forged round bar  $1\frac{1}{2}$  in. in diam. In addition to the 30 pct Zn  $\alpha$ -brass supplied, one other brass was made of nominal composition 20 pct Zn; this was made from

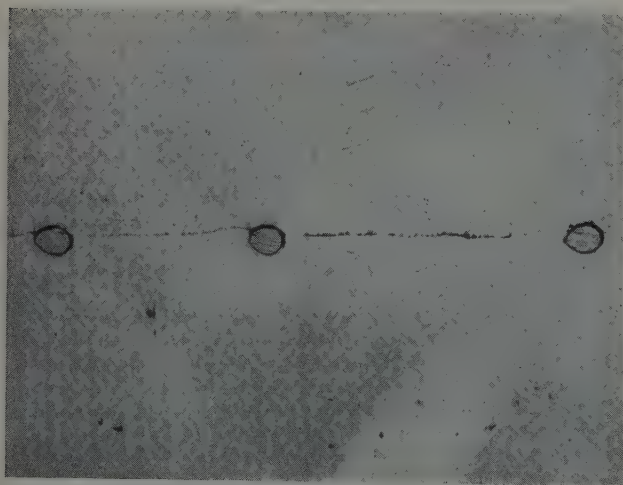
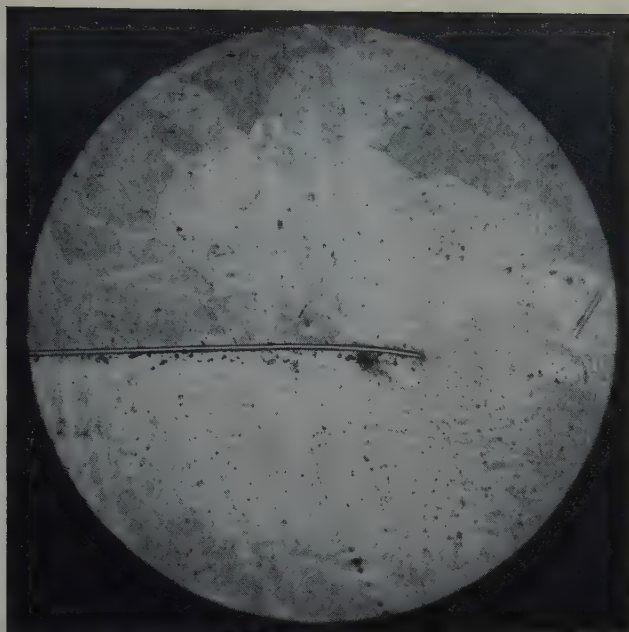
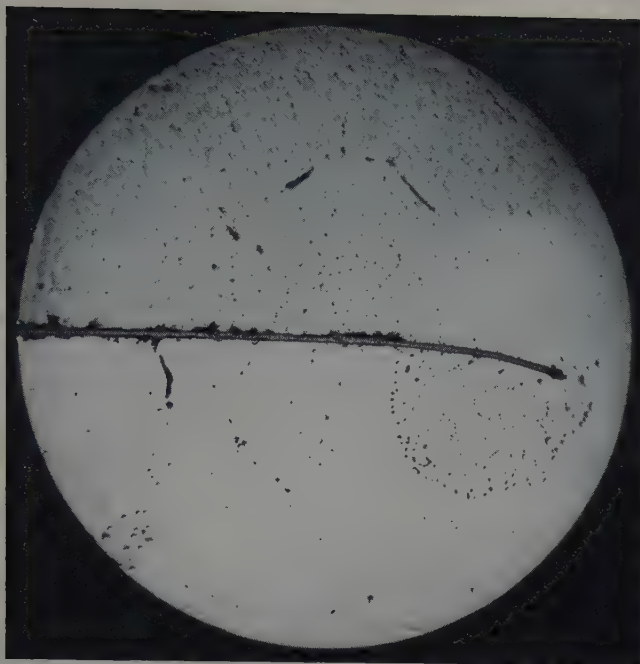


Fig. 3—Imperfect weld showing wire markers and imperfectly welded join. X100. Reduced approximately 33 pct for reproduction.





ance elements; mechanical pressure was applied to the disks, through steel rods as shown; vacuum or controlled pressures of any desired gas was maintained through pump and manometer control. The heating element was Kanthal; rapid heating was possible—the disks could be brought to a welding temperature in 20 min; the temperature was kept constant during welding by a Celec tray control. Other details in the welding operation are obvious from Fig. 2. The thermocouple registered nominal temperatures only; these were high, approximating the melting point of the low-melting alloy; but the disks, held between steel plates, were actually at a substantially lower temperature; the thermocouple served only as a guide to reproduce the welding operation; the actual temperatures of the disks were not measured.

After welding, the specimens were machined with very great care, using a very sharp tool, the last layers removed were never thicker than 0.008 in., in order to minimize distortion, to produce two opposite planes accurately perpendicular to the welding zone and the marker; in the case of foil markers, four such surfaces were produced, related by right angles. This machining served two purposes: to reveal faulty welds on microscopic examination (whence many faulty specimens were discarded) and to provide an opportunity to establish the initial marker position. In the case of Cu-Zn alloys, this machining was deep enough to remove completely any dezincified outer layer. Fig. 3 shows the position of the wire marker with respect to the weld join (in an imperfect weld); other figures herein illustrate the weld zone in properly welded specimens. The inter-marker distance was determined with a comparator capable of yielding measurements reproducible within 0.0004 cm. Microscopic inspection showed the markers to be effectively equally imbedded in the opposing disks; the line of weld could be readily recognized.

#### Diffusion Treatments

The welded disk composites, when including brass, were annealed for diffusion in a steel container packed with brass chips (of the same composition as that in the disk composite) and lampblack (to prevent sticking of the charge), in order to avoid de-

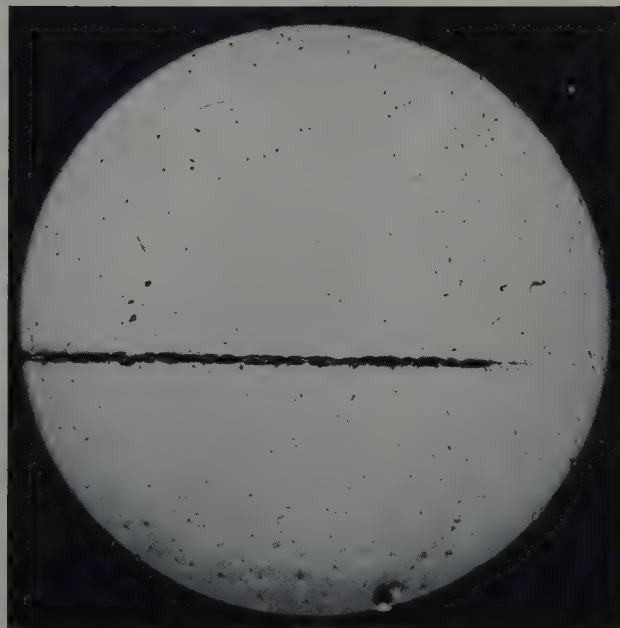


Fig. 4 (upper left)—Sample C1 with foil marker after diffusion, unetched. X25.

Fig. 5 (upper right)—Sample E1 with foil marker after diffusion, etched. X25.

Fig. 6 (lower right)—Sample C3 with foil marker after diffusion showing final straightening of foil after prolonged diffusion.

zincing. As a result the Cu disks in all such composites were uniformly coated with a layer of brass, and the whole sample thus presented to the ambient a surface of the same composition, that of the high-Zn disk. For other disk composites hydrogen was used in general; Cu-Al alloys heated in hydrogen were observed to swell, perhaps because of hydrogen reduction of included oxides, and for this system nitrogen was used as a protective atmosphere. Cu-Al and Cu-Ni alloys were annealed in vacuum. Diffusion temperatures were maintained to  $\pm 2^\circ\text{C}$ .

#### Measurements on Diffused Couples

After diffusion, the flat longitudinal planes were re-machined, with similar care, in the case of Cu-Zn alloys this machining sufficed to remove completely

Table III. Displacement of Interface Markers

| Specimen            | Type of Markers at Each Interface                                                                                                                                                                                                                        | Temp, °C | Time of Diffusion, hr             | Shift at Each Interface, cm                              | Method of Measurement                                       | Observations                                                                                                            |
|---------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|-----------------------------------|----------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| <b>Cu-Zn System</b> |                                                                                                                                                                                                                                                          |          |                                   |                                                          |                                                             |                                                                                                                         |
| B 20                | 3 W wires<br>0.0050 cm                                                                                                                                                                                                                                   | 800      | 119                               | 0.0109                                                   | Diff. curve                                                 | From B 20-I                                                                                                             |
| B 35                | 5 Mo wires<br>0.0075 cm                                                                                                                                                                                                                                  | 784      | 157<br>691<br>691<br>691          | 0.0038<br>0.0110<br>0.0086<br>0.0082                     | Direct<br>Direct<br>Diff. curve<br>Diff. curve              | From B 35-II<br>From B 35-I                                                                                             |
| B 36                | 5 Mo wires<br>0.0075 cm                                                                                                                                                                                                                                  | 834      | 119<br>289<br>507<br>507          | 0.0076<br>0.0115<br>0.0180<br>0.0190                     | Direct<br>Direct<br>Direct<br>Diff. curve                   | From B 36-II                                                                                                            |
| B 37                | 5 Mo wires<br>0.0075 cm                                                                                                                                                                                                                                  | 885      | 97<br>197<br>197                  | 0.0105<br>0.0146<br>0.0148                               | Direct<br>Direct<br>Diff. curve                             | Average from<br>B 37-I and<br>B 37-II                                                                                   |
| B 42                | 3 Mo wires<br>0.0075 cm<br>and<br>2 Fe foils<br>0.0025 cm                                                                                                                                                                                                | 784      | 123<br>123<br>245<br>533<br>533   | 0.0067<br>0.0048<br>0.0105<br>0.0155<br>0.0094           | Direct<br>Direct<br>Direct<br>Direct<br>Foil bend           | Total shift<br>Rel. to foils<br>Total shift<br>(Foils irregular)<br>Total shift                                         |
| B 45                | 3 Mo wires<br>0.0075 cm<br>and<br>2 Ta foils<br>0.0025 cm                                                                                                                                                                                                | 883      | 19<br>19<br>85<br>85<br>85<br>185 | 0.0059<br>0.0047<br>0.0127<br>0.0105<br>0.0089<br>0.0180 | Direct<br>Direct<br>Direct<br>Direct<br>Foil bend<br>Direct | Total shift<br>Rel. to foils<br>Total shift<br>Rel. to foils<br>Total shift<br>(Foil reference lost)                    |
| C 1                 | 3 Mo wires<br>0.0075 cm<br>and<br>1 Fe foil<br>0.0025 cm<br>and<br>1 Ta foil<br>0.0025                                                                                                                                                                   | 882      | 19<br>19<br>85<br>157<br>257      | 0.0052<br>0.0035<br>0.0075<br>0.0084<br>0.0089           | Direct<br>Direct<br>Direct<br>Direct<br>Direct              | Total shift<br>Rel. to Ta foil<br>(Zn crossed Fe foil)<br>Total shift<br>Total shift<br>(Foil ref. lost)<br>Total shift |
| C 3                 | 3 Mo wires<br>0.0075 cm<br>and<br>1 Fe foil<br>0.0025 cm<br>and<br>1 Ta foil<br>0.0025 cm                                                                                                                                                                | 883      | 72<br>167<br>267                  | 0.0052<br>0.0066<br>0.0085                               | Direct<br>Direct<br>Direct                                  | Total shift<br>(Foil ref. lost)<br>Total shift<br>Total shift                                                           |
| C 11                | 3 Mo wires<br>0.0075 cm<br>and<br>2 Pt foils<br>0.0050 cm                                                                                                                                                                                                | 882      | 19<br>85                          | 0.0050<br>0.0089                                         | Direct<br>Direct                                            | Total shift<br>(Pt foils dissolved)<br>Total shift                                                                      |
| C 14                | 3 W wires<br>0.0012 cm<br>and<br>2 Mo wires<br>0.0075 cm<br>3 Pt wires<br>0.0050 cm                                                                                                                                                                      | 884      | 66<br>112                         | 0.0027<br>0.0040                                         | Direct<br>Direct                                            | Total for Mo, W<br>(Pt wires dissolved)<br>Total for Mo, W                                                              |
| C 17                | 2 Mo wires<br>0.0075 cm<br>2 Ni wires<br>0.0075 cm<br>1 Pt wire<br>0.0012 cm                                                                                                                                                                             | 923      | 66                                |                                                          |                                                             | Cu/20Zn brass/Cu<br>(Sample visibly<br>expanded due to<br>gas reaction)                                                 |
| C 19                | 2 sets of<br>Fe foils<br>in brass<br>disks, per-<br>pendicularly<br>to interface                                                                                                                                                                         | 884      | 73                                | 0.0007                                                   | Direct                                                      | Lateral change<br>in dimensions<br>of the brass,<br>at the interface                                                    |
| C 20                | Wires:<br>2 Mo-0.0075 cm<br>2 W-0.0050 cm<br>2 Ni-0.0075 cm<br>2 Pt-0.0012 cm<br>Foils:<br>1 Fe-0.0025 cm<br>1 Pt-0.0050 cm<br>1 Ni-0.0050 cm<br>1 Ta-0.0025 cm<br>Others:<br>Fe <sub>2</sub> O <sub>3</sub><br>Al <sub>2</sub> O <sub>3</sub><br>Carbon | 884      | 27                                | 0.0024                                                   | Direct                                                      | Total, for all<br>markers<br>(All foils<br>except one Ta<br>were crossed<br>by Zn or dissolved)                         |



Table III, Cont. Displacement of Interface Markers

| Specimen                        | Type of Markers at Each Interface                         | Temp, °C | Time of Diffusion, hr | Shift at Each Interface, cm | Method of Measurement | Observations        |
|---------------------------------|-----------------------------------------------------------|----------|-----------------------|-----------------------------|-----------------------|---------------------|
| E 1                             | 3 Mo wires<br>0.0075 cm<br>2 Ta foils<br>0.0025 cm        | 884      | 46                    | —0.0027                     | Direct                | Total for wires     |
|                                 |                                                           |          | 46                    |                             |                       |                     |
|                                 |                                                           |          | 46                    | + 0.0025                    | Direct                | Total for foils     |
|                                 |                                                           |          | 46                    | —0.0052                     | Direct                | Rel. to foils       |
|                                 |                                                           |          | 46                    | —0.0079                     | Foil bend             |                     |
| C 22                            | 2 Mo wires<br>0.0075<br>2 Pt wires                        | 733      | 2                     | + 0.0065                    | Direct                | Total for Mo wires  |
|                                 |                                                           |          | 2                     | —0.0196                     | Direct                | Total for interface |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          | 18.8                  | + 0.0210                    | Direct                | Total for Mo wires  |
|                                 |                                                           |          | 18.8                  | —0.0685                     | Direct                | Total for interface |
| Cu-Al System                    |                                                           |          |                       |                             |                       |                     |
| B 34                            | 5 Mo wires<br>0.0075 cm                                   | 948      | 147                   | 0.0014                      | Direct                | Total shift         |
|                                 |                                                           |          |                       | 0.0015                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          | 341                   | 0.0022                      | Direct                | Total shift         |
|                                 |                                                           |          |                       | 0.0021                      | Direct                | Total shift         |
| B 39                            | 5 Mo wires<br>0.0075 cm                                   | 889      | 305                   | 0.0024                      | Direct                | Total shift         |
|                                 |                                                           |          |                       | 0.0022                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| C 6                             | 5 W wires<br>0.0012 cm                                    | 994      | 186                   | 0.0011                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| Cu-Zn System                    |                                                           |          |                       |                             |                       |                     |
| B 23                            | 4 W wires<br>0.0050 cm                                    | 804      | 224                   | 0.0029                      | Direct                | Total shift         |
|                                 |                                                           |          |                       | 0.0031                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| B 28                            | 4 Mo wires<br>0.0075 cm                                   | 812      | 164                   | 0.0026                      | Direct                | Total shift         |
|                                 |                                                           |          |                       | 0.0030                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| B 41                            | 5 Mo wires<br>0.0075 cm<br>and<br>2 Fe foils<br>0.0025 cm | 733      | 191                   | 0.0002                      | Direct                | Total, uncorrected  |
|                                 |                                                           |          |                       | 0.0012                      | Direct                | Rel. to foils       |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          | 695                   | 0.0020                      | Direct                | Total, uncorrected  |
|                                 |                                                           |          |                       | 0.0024                      | Direct                | Rel. to foils       |
| B 46                            | 3 Mo wires<br>0.0075 cm                                   | 733      | 504                   | 0.0023                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| Cu-Ni, Ag-Au, and Cu-Au Systems |                                                           |          |                       |                             |                       |                     |
| B 38                            | 3 Mo wires<br>0.0075 cm                                   | 947      | 362                   | 0.0039                      | Diff. curve           |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| C 4                             | 3 Mo wires<br>0.0075 cm                                   | 1054     | 312                   | 0.0094                      | Direct                | Total shift         |
|                                 |                                                           |          |                       | 0.0140                      | Diff. curve           | From C 4-I          |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| C 21                            | 2 Mo wires<br>0.0075 cm                                   | 839      | 24½                   | 0.0007                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          | 92                    | 0.0020                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
| D 2                             | 4 W wires<br>0.0012 cm                                    | 910      | 96                    | 0.0113                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
| D 3                             | 3 Mo wires<br>0.0075 cm                                   | 925      | 50                    | 0.0113                      | Direct                | Total shift         |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |
|                                 |                                                           |          |                       |                             |                       |                     |

the outer layer which had absorbed Zn. The surfaces then were polished and etched; samples revealing faulty welds were discarded. The markers (and sometimes the original join) were visible on the final surface.

The diffusion-penetration curves (herein designated as *c-x* curves whatever units were used to express concentration and distance) were obtained from samples procured by machining. Machining was a critical operation; accurate specimen alignment with the lathe axis was obtained by the use of a mounted telescope with reticule, sighting upon the readily visible markers, rotating the specimen and adjusting; in some cases the weld line on an etched sample served equally well. Successive layers were machined normal to the lathe axis (parallel to the markers and join); the thickness of layers varied with the extent of diffusion; with small amounts of diffusion, and with nearly symmetrical diffusion-penetration curves, it was 0.0050 cm, or 0.0075 cm; in others, these same thicknesses were taken when the *c-x* curve varied sharply with distance, but when it varied but slowly thicker layers, 0.0150 and 0.0200 cm, were taken. The machined layers were analyzed chemically; in the Cu-Zn system usually Cu only was determined by chemical analysis, though both Cu and Zn were determined in sample

B20-II. Some 20 machined samples were analyzed for each *c-x* curve.\*

#### Measurement of Marker Position and Marker Shift

**Direct Method:** The initial distances between markers in double couples (sandwiches) were established after welding as noted above; after diffusion these distances were determined again in the same way; this is effectively the method employed by Smigelskas and Kirkendall<sup>1</sup>; it is denoted herein as the "direct method"; as in Figs. 47 to 55 and Table III these were reproducible to  $\pm 0.0004$  cm; since the markers were pressed between the metal disks before welding, the wires were imbedded in both disks (in Smigelskas and Kirkendall's electroplating technique the wires were not centered exactly at the join, but lay just off the join, imbedded in the electroplate); it was easy to locate the wires with respect to the welded join, and to observe the penetration of the disks by the markers, Fig. 3; in the Cu/ $\alpha$ -brass couples, the wires penetrated the Cu a little more than the  $\alpha$ -brass. Microscopic inspection showed that inclusions at the join move as do the markers; they thus also serve as markers. The

\* For the data from which *c-x* curves were plotted order Document 3115 from American Documentation Institute, 1719 N St., N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 in. high on standard 35 mm motion picture film) or \$1.05 for photocopies (6x8 in.) readable without optical aid.

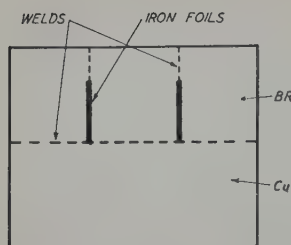
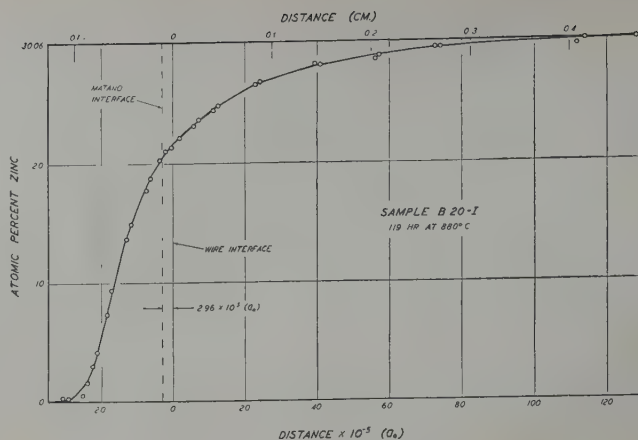


Fig. 7 (left)—Showing placement of foil markers for measurement of changes in lateral dimensions.



direct method is not the best (as the data will show), for it probably suffers from secondary effects of creep, internal gas reactions, and possibly, though not certainly, dimensional changes resulting from internal stresses and recrystallization.

*Diffusion Curve Method:* The procedure of machining layers to determine the  $c$ - $x$  curve served to place the markers upon the  $c$ - $x$  curve, for when the markers were encountered during machining they could be recognized readily and thus associated with the composition of the layer machined at that point. The accuracy of the placement of the markers by this method was thus that of the thickness of the machined layer. As shown elsewhere, the position of the Matano interface was found to agree with the position of the original join, when lattice space is

Table IV. Matano Areas Observed in the Specimens Studied

| Specimen  | Time, hr | Temp, °C | Matano Area<br>(cm) (A/o) |
|-----------|----------|----------|---------------------------|
| B 20-I    | 119      | 880      | 0.95                      |
| B 35-I,II | 691      | 784      | 0.98                      |
| B 36-II   | 507      | 834      | 1.33                      |
| B 37-I,II | 197      | 885      | 1.36                      |
| B 22-I    | 165      | 977      | 0.99                      |
| B 34-I    | 608      | 948      | 1.09                      |
| B 39-I    | 305      | 889      | 0.59                      |
| B 23-I    | 224      | 804      | 0.10                      |
| B 33-I    | 524      | 808      | 0.16                      |
| B 46-I    | 504      | 733      | 0.07                      |
| B 38      | 362      | 947      | 0.51                      |
| C 4-I     | 312      | 1054     | 0.96                      |

employed; thus the difference in position of the marker and the Matano interface is the shift; this method is denoted herein as the “diffusion curve method,” see Figs. 47 to 55 and Table III. A single couple will suffice for this method.

*Foil Reference Method:* Impermeable foils inserted in the original join served as reference points for other, mobile markers; as noted elsewhere, this is a good method, for if the movement of the mobile markers is corrected for the (slight) movement of the centers of the "static" foils, then secondary effects of creep, etc., are excluded. In Figs. 47 to 55 and Table III, this is denoted as the "relative to foil" method.

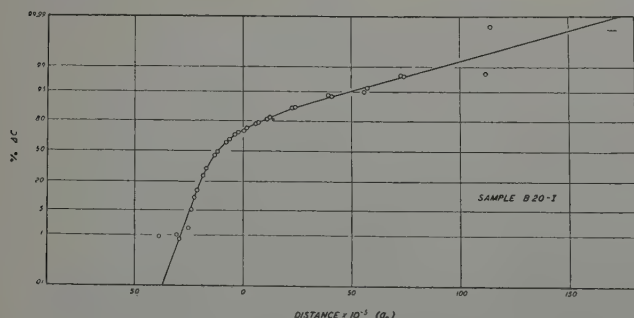


Fig. 8—Probability plot of C-X curve for sample B20-1.

*Foil Bend Method:* This method is based upon the new observation that the edge of a foil placed at the join will bend progressively as diffusion occurs around it, Figs. 4 and 5. The middle portion of the "impermeable" foil will stay fixed as long as it is not affected by the diffusion occurring around the edges.

This also appears to give a reliable experimental method for obtaining the shift of markers caused by diffusion, since the movement of the foil tip can be measured (with respect to the unaffected middle portion) and such a measurement will not be affected by secondary volume changes occurring in the disks themselves. This method is denoted as the "foil bend method" in Figs. 47 to 55 and Table III. Interestingly enough, on very extensive diffusion, when diffusion had extended thoroughly around the foil, the foil "unbent," becoming flat again, Fig. 6.

### Measurement of Shift in Lateral Dimensions

All treatments of the work of Smigelskas and Kirkendall (and of other work) assume that there is no change in lateral dimensions, i.e., perpendicular to the direction of the diffusion current, though there have been no measurements of this. This measurement was made on a multiple sandwich, sample C19, with foils placed parallel to the diffusion direction, as sketched in Fig. 7. Three blocks of 30 pct Zn brass were welded with two iron foils placed as shown; this specimen then was machined to produce a plane surface perpendicular to the foil markers and then welded to a copper disk. Movement of these markers, spaced at a distance of 1.05 cm with respect to one another, served to evaluate

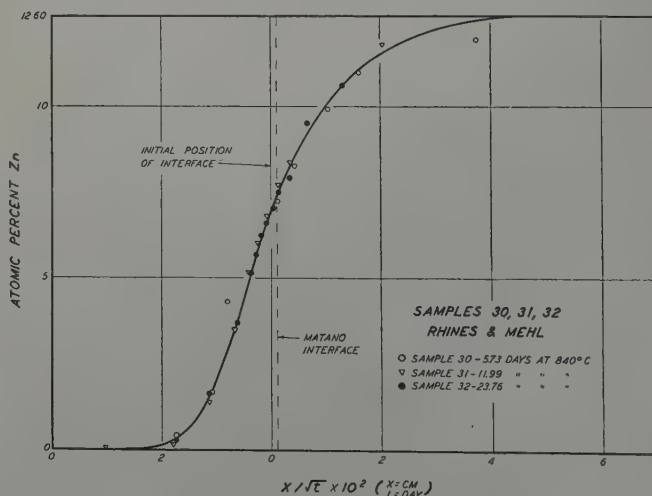


Fig. 10—Plot of three C-x curve for Cu/ $\alpha$ -brass couples for different values of time, abscissas  $x t^{1/2}$ .



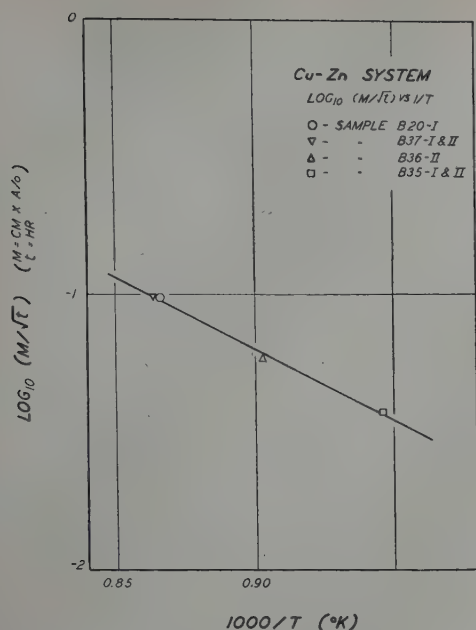
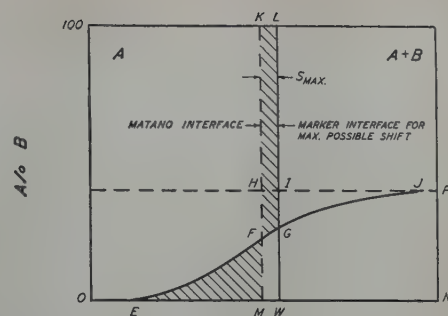


Fig. 11 (left)—Log  $Mt^{1/2}$  vs.  $1/T$ , Cu/ $\alpha$ -brass couples.

Fig. 12 (right)—Graphical determination of maximum possible marker shift.



serves to “normalize” the curve—it is much easier to draw a “best fit,” to eliminate clearly spurious points. The curve drawn can then be used to re-draw the conventional curve (Fig. 9), and to calculate  $D = f(c)$ ; this is the method adopted in all cases.

Diffusion in solids occurs in a lattice; atomically, it appears that the process must consist of atom jumps from one lattice point to another, the distance of closest approach of atoms; it is unlikely that this elementary process should involve a multiple of this distance. Whatever the distance, movement must occur in steps in lattice space, which may be taken as the side of the unit cell,  $\bar{a}_0$  (or the distance of closest approach). Cartesian space is thus indirect in the process; advantages should accrue to plotting lattice space (or distance) instead of Cartesian space (or distance) and this method has been adopted. Such a plot obviously avoids the necessity for any correction of distance measured at room temperature to distance at the temperature of diffusion; on this basis a comparison of  $D$  at one concentration with  $D$  at another should be more fundamental. In studying marker displacement, this method has a special advantage: marker displacements originating in density changes are eliminated. The transformation from distance in terms of centimeters to distance in terms of the number of lattice ( $\bar{a}_0$ ) spacings, can readily be accomplished graphically; Fig. 9 is drawn on this basis. Diffusion coefficients calculated from such curves will have the dimensions  $(\bar{a}_0)^2$  per sec. The ordinate should be the number of atoms in the unit cell, although, since atomic percentage is linearly related to this in substitutional solid solutions, atomic percentage may be used. This method of plotting has been used wherever the precision of the data seemed to warrant the labor.

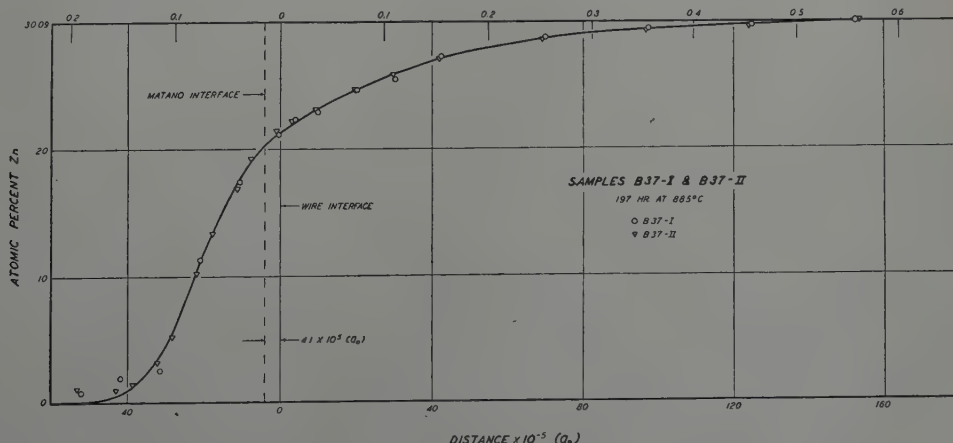
Since the present work is primarily a general experimental exploration of marker shift, only a few measurements were made on the rate of marker movement at one temperature (known from Smigelskas and Kirkendall<sup>1</sup> and Darken<sup>4</sup> to be parabolic);

lateral dimensional change. Measurements were made between the foils very near the interface and at a point well beyond the diffusion zone; some movement might be expected in the latter because of creep, etc.; the lateral shift is taken as the difference between the movements of the foils at the interface and those beyond the diffusion zone. The diffusion temperature was 884°C and the time 73 hr. Diffusion-penetration curves were not made, but can be calculated from the other data for this system.

### Methods of Plotting Results

The  $c$ - $x$  curves are plotted conventionally as concentration, either in weight or atomic percentage, vs. distance in usual units. As is well known (see, for example, ref. 9), if the diffusion coefficient  $D$  does not vary with the concentration, this plots as a straight line on probability paper; if  $D$  varies with concentration ( $D = f(c)$ ) the curve is bent, as in all cases herein. Such a plot, however (Fig. 8),

Fig. 13— $c$ - $x$  curve and marker position for samples B37-I and II, Cu/ $\alpha$ -brass.



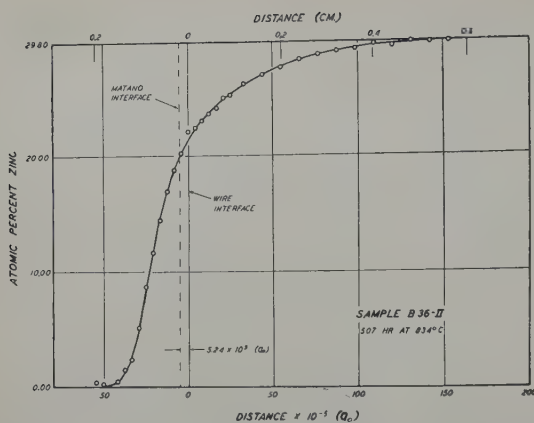


Fig. 14—C-X curve and marker position for sample B36-II, Cu/α-brass.

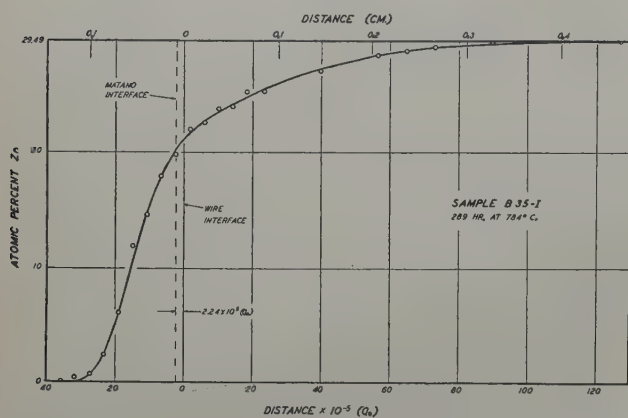


Fig. 15—C-X curve and marker position for sample B35-I, Cu/α-brass.

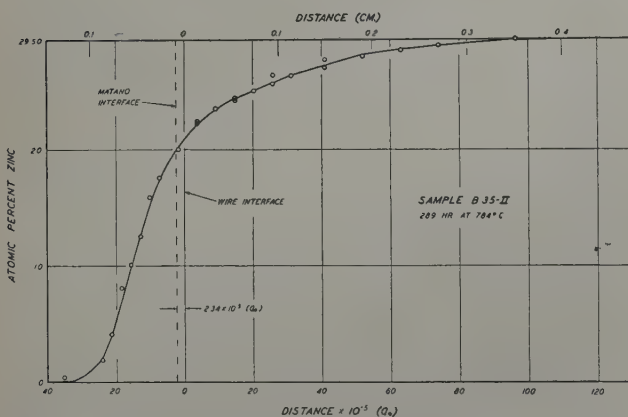


Fig. 16—C-X curve and marker position for sample B35-II, Cu/α-brass.

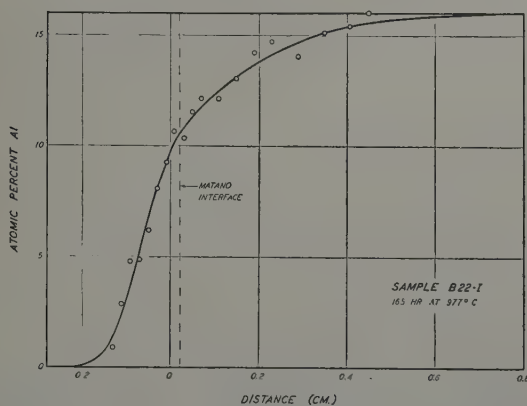


Fig. 17—C-X curve and marker position for sample B22-I, Cu/αCu-Al.

Table VI. Marker Shifts and Matano Areas

| Specimen            | Matano Area (cm) (A/o) | Shift of markers (cm) | Observations     |
|---------------------|------------------------|-----------------------|------------------|
| <b>Cu-Zn System</b> |                        |                       |                  |
| B 20                | 0.98                   | 0.0109                | From diff. curve |
| B 35                | 0.96                   | 0.0084                | From diff. curve |
| B 36                | 1.34                   | 0.0190                | From diff. curve |
| B 37                | 1.29                   | 0.0148                | From diff. curve |
| B 42                | 0.42                   | 0.0048                | Rel. to foils    |
|                     | 0.85                   | 0.0094                | Foil bending     |
| B 45                | 0.40                   | 0.0047                | Rel. to foils    |
|                     | 0.84                   | 0.0105                | Rel. to foils    |
|                     | 0.84                   | 0.0089                | Foil bending     |
| C 1                 | 0.40                   | 0.0035                | Rel. Ta foil     |
| E 1                 | 0.62                   | 0.0052                | Rel. to foils    |
|                     | 0.62                   | 0.0079                | Foil bending     |
| <b>Cu-Al System</b> |                        |                       |                  |
| B 34                | 0.72                   | 0.0014                | Total shift      |
|                     | 1.11                   | 0.0021                | Total shift      |
|                     | 1.48                   | 0.0023                | Total shift      |
| B 39                | 0.60                   | 0.0011                | Total shift      |
| C 6                 | 1.21                   | 0.0026                | Total shift      |
| <b>Cu-Sn System</b> |                        |                       |                  |
| B 23                | 0.102                  | 0.0030                | Total shift      |
| B 28                | 0.094                  | 0.0028                | Total shift      |
| B 41                | 0.046                  | 0.0012                | Rel. to foils    |
|                     | 0.087                  | 0.0024                | Rel. to foils    |
| B 46                | 0.072                  | 0.0023                | Total shift      |
| <b>Cu-Ni System</b> |                        |                       |                  |
| B 38                | 0.51                   | 0.0039                | From diff. curve |
| C 4                 | 0.96                   | 0.0140                | From diff. curve |
|                     |                        | 0.0094                | Direct measure   |
| <b>Ag-Au System</b> |                        |                       |                  |
| D 2                 | 3.4K                   | 0.0113                | Direct measure   |
| D 3                 | 2.7K                   | 0.0113                | Direct measure   |

a variety of temperatures and times was used. It would be useful to have a method to compare the results obtained. An approximate method has been derived and will be employed in treating some of the data.

The penetration  $x$ , for a given concentration, ( $c$ ), depends upon time, as is well known, by the relation:

$$x(c) = k(c) \cdot t^{1/2}$$

Since all points in a diffusion curve obey this relation, it is obvious that, from a single diffusion curve for a given time, the diffusion curve corresponding to any other time (at the same temperature) may be derived. The inverse, of course, is also true: we can reduce all diffusion curves (for different times, at a given temperature) to a single master curve, if instead of distance  $x$  we plot  $(x \cdot t^{-1/2})$ , Fig. 10 (plotted from the data of Rhines and Mehl<sup>10</sup>).

If we wish to compare diffusion curves (or shifts) obtained at different temperatures, the following approximate treatment may be used:

The usual expression for  $D$ :

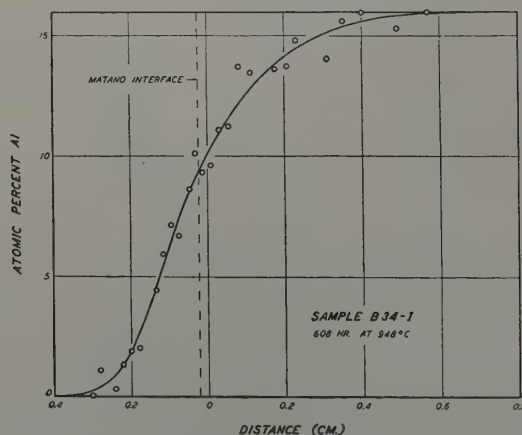


Fig. 18—C-X curve and marker position for sample B34-I, Cu/αCu-Al.



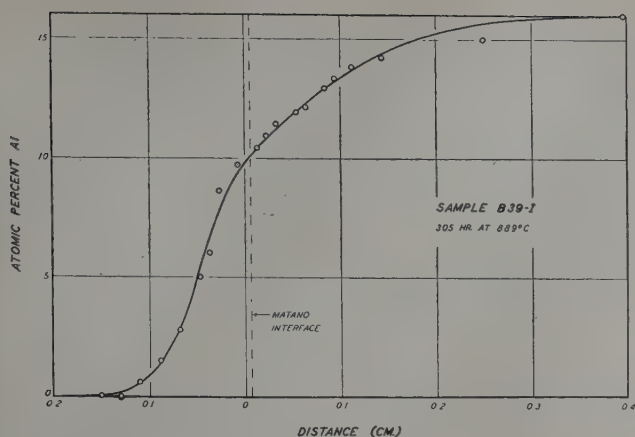


Fig. 19—C-X curve and marker position for sample B39-I, Cu/αCu-Al.

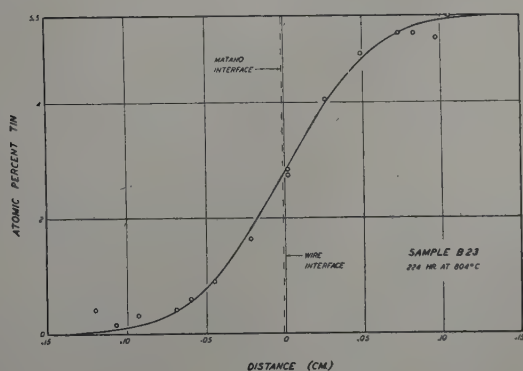


Fig. 20—C-X curve and marker position for sample B23, Cu/αCu-Sn.

$$D = A \cdot e^{-Q/RT}$$

can be written:

$$D(c,T) = A(c) \cdot e^{-\frac{Q(c)}{RT}} \quad [1]$$

indicating that, for a given solid solution,  $D$ ,  $A$ , and  $Q$  depend on the concentration. If we are dealing with relatively small temperature intervals, or if we are satisfied with only an approximate treatment, we may substitute an average, constant value  $Q_{av}$  for the function  $Q(c)$ :

$$D(c,T) = A(c) \cdot e^{-\frac{Q_{av}}{RT}} \quad [2]$$

Consequently, if we know the function  $D(c,T)$  for a temperature  $T_1$ , its value at  $T_2$  is given by:

$$D_2(c) = e^{\frac{Q_{av}}{R} \cdot \frac{T_2 - T_1}{T_2 T_1}} \cdot D_1(c) \quad [3]$$

which is equivalent to the displacement of  $D = f(c)$  by a constant amount:

$$D_2(c) = K \cdot D_1(c) \quad [4]$$

In this treatment, then, passage from temperature  $T_1$  to  $T_2$  is equivalent to multiplying the coordinates  $x$  of the diffusion curve by a constant  $\sqrt{K}$ .

Thus, we may write, as an approximation (eq 3 above):

$$D_2(c) = e^{\frac{Q_{av}}{R} \cdot \frac{T_2 - T_1}{T_2 T_1}} \cdot D_1(c) \quad [3a]$$

and

$$x_2(c) = e^{\frac{Q_{av}}{2R} \cdot \frac{T_2 - T_1}{T_2 T_1}} \cdot x_1(c) \quad [5]$$

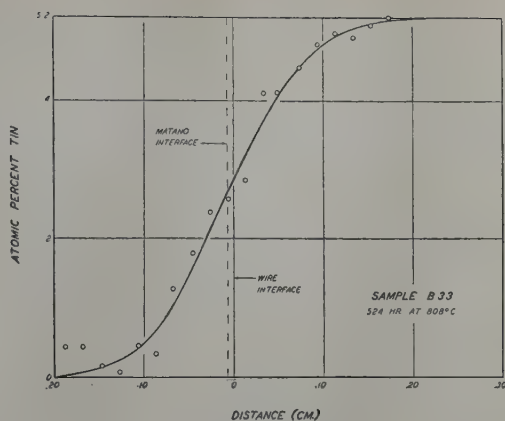


Fig. 21—C-X curve and marker position for sample B33, Cu/αCu-Sn.

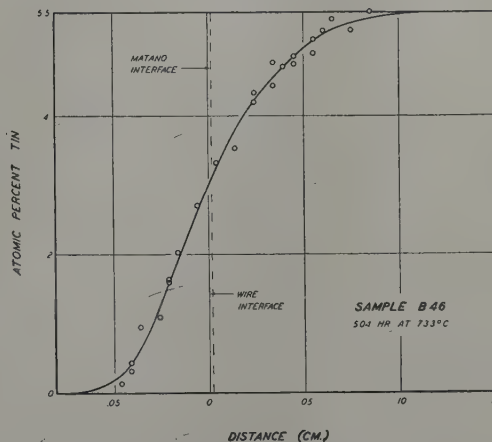


Fig. 22—C-X curve and marker position for sample B46, Cu/αCu-Sn.

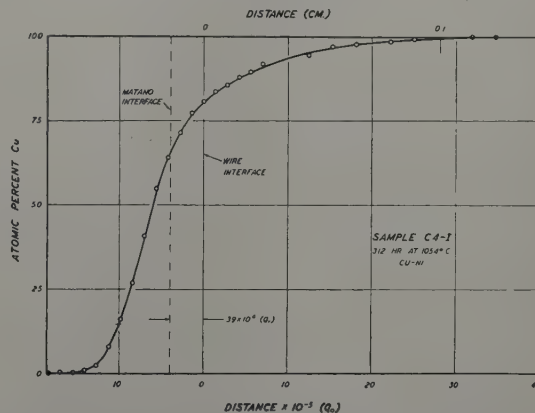


Fig. 23—C-X curve and marker position for sample C4-I, Cu-Ni.

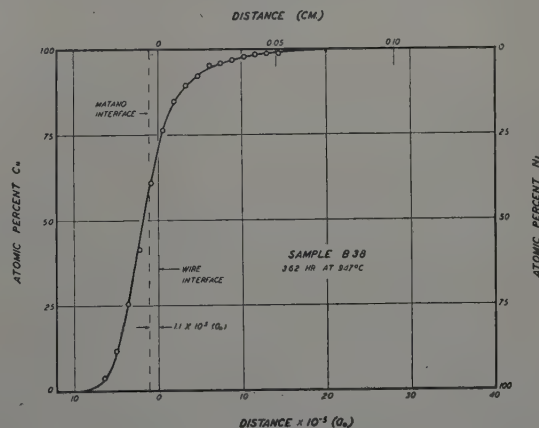


Fig. 24—C-X curve and marker position for sample B38, Cu-Ni.

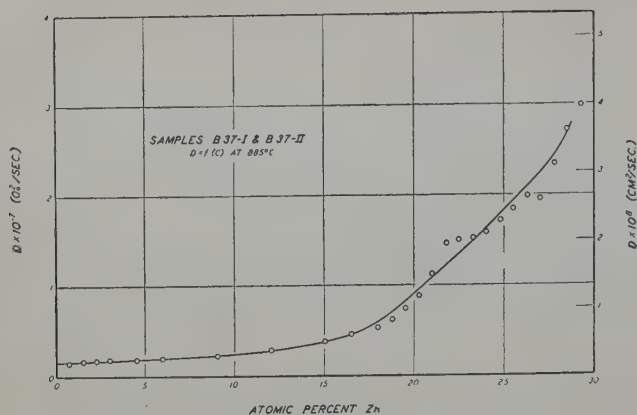


Fig. 25— $D = f(c)$  for samples B37-I, II, Cu/ $\alpha$ -brass.

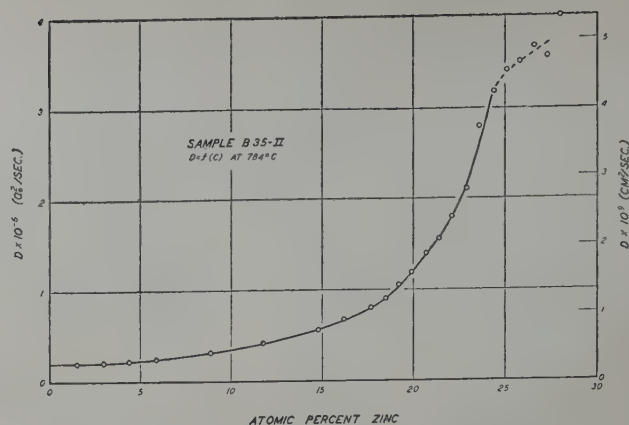


Fig. 29— $D = f(c)$  for sample B35-II, Cu/ $\alpha$ -brass.

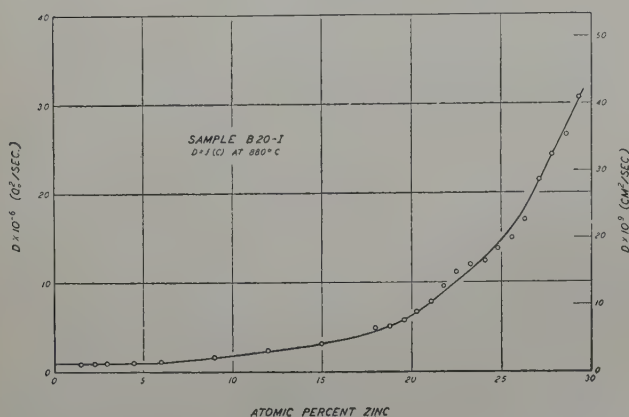


Fig. 26— $D = f(c)$  for sample B20-I, Cu/ $\alpha$ -brass.

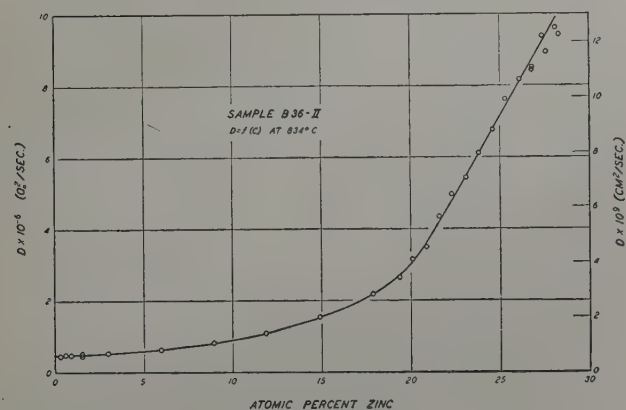


Fig. 27— $D = f(c)$  for sample B36-II, Cu/ $\alpha$ -brass.

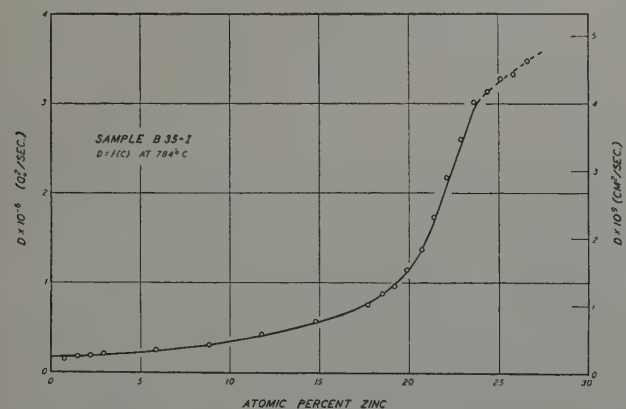


Fig. 28— $D = f(c)$  for sample B35-I, Cu/ $\alpha$ -brass.

If the time also varies, then:

$$x_2(c) = \sqrt{\frac{t_2}{t_1}} \cdot e^{\frac{Q_{av}}{2R} \cdot \frac{T_2 - T_1}{T_2 T_1}} \cdot x_1(c) \quad [6]$$

or, in general:

$$x(c) = K(c) \cdot t^{1/2} \cdot e^{-\frac{Q_{av}}{2RT}} \quad [7]$$

This is approximate, but it predicts the actual shape of the diffusion curve quite well, knowing the diffusion curve for a given  $t$  and a given  $T$ .

The Boltzmann-Matano area (hereinafter the "Matano area") is that on either side of the Boltzmann-Matano interface (the "Matano interface"). These areas, as measured from the diffusion curves, are given in Table IV. This area measures the amount of diffusion; if atoms are conserved on lattice points, it represents the number of atoms diffused. It varies linearly with  $x$  and  $t^{1/2}$  and can be written:

$$M = K_M \cdot t^{1/2} \cdot e^{-\frac{Q_M}{2RT}} \quad [8]$$

Again  $Q$  is averaged over a concentration range. This area is less subject to error since slopes and small areas are not measured, as they are in calculating  $D$ .

The values of  $K_M$  and  $Q_M$  in eq 8 may be obtained from a plot of  $\log_{10}(M/t^{1/2})$  vs.  $1/T$ , employing the data from Table IV; Fig. 10 gives the plot for the system Cu-Zn (similar plots were made for the other systems); the plots serve to show that eq 8 is satisfactory; the derived values for  $K_M$  and  $Q_M$  are given in Table V. Using eq 8 and the data in Table V, the Matano areas have been calculated for those specimens in which marker displacements have been measured; these marker displacements and corresponding Matano areas are given in Table VI. These are the data used in Figs. 11 to 15; since the marker shift varies with  $t^{1/2}$ , it should also vary linearly with the Matano area.

In the Ag-Au system values of  $K_M$  and  $Q_M$  were not available, the comparison of the two measured shifts was approximated by assuming a  $Q$ -value of 26,600 cal per mol.<sup>11</sup> This value may be too low.

### Maximum Possible Shift

If it is assumed, as others have, that the marker shift results from unequal countercurrent diffusion flow, it is possible to calculate, in some of the present cases, the marker displacement that would result if the diffusion coefficient of one of the atomic species were zero—if one of the atomic species did not cross the marker at all. This shift will be desig-



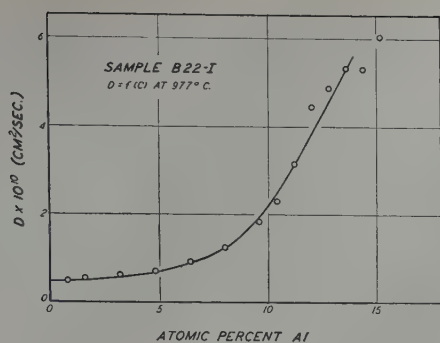


Fig. 30— $D = f(c)$  for sample B22-I,  
Cu/ $\alpha$ Cu-Al.

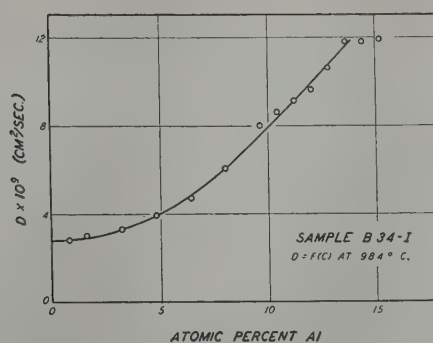


Fig. 31— $D = f(c)$  for sample B34-I,  
Cu/ $\alpha$ Cu-Al.

nated as the "maximum possible shift,"  $S_{\max}$ . Such a calculation assumes that no measurable voids are created, and that all dimensional changes are in the direction of diffusion flow.

Fig. 12 represents a diffusion curve in lattice units, for diffusion between a metal and its terminal solid solution. Areas in this diagram are proportional to numbers of atoms. At the outset, the number of B atoms is proportional to the area MHPN. If B atoms cross the markers toward the left without any A atoms crossing toward the right, the markers will move to a new position WL in such a way that the area EFM and FKLK will be equal. The maximum possible shift would then be the shift from MK to WL. The values of  $S_{\max}$  in terms of lattice units are then reconverted to cm, and plotted against cm, as in Figs. 48 to 53.

### c-x Curves

The data are plotted in Figs. 9 and 13 to 24; the abscissas are lattice spacings where possible. As noted, Fig. 13 plots data for both couples in a sandwich; the correspondence speaks well for the reproducibility of such data.

$$D = f(c)$$

From the above curves, the variation of  $D$  with concentration can be plotted ( $D = f(c)$ ); the results are plotted in Figs. 25 to 36. Fig. 37 is a comparison of the  $D = f(c)$  curve for the Cu/20 pct Zn couple, as determined at 923°C as compared with a similar curve for the couple Cu/30 pct Zn, extrapolated from the curves for this couple obtained at lower temperatures. In the Cu/20 pct Zn couple, the  $D$ -values above about 10 pct Zn are for compositions losing Zn during diffusion, below 10 pct Zn for compositions gaining Zn. In the Cu/30 pct Zn couple the dividing composition is about 15 pct. The curves suggest that for a given composition, the  $D$ -value is the higher when that composition is losing Zn than when gaining, as though the act of losing Zn creates a structural degeneracy which favors a higher mobility. Fig. 38 is a recalculation of the earlier data of Rhines and Mehl,<sup>10</sup> for somewhat similar couples. The results are essentially the same. This result is highly tentative, for the comparison for the Cu/20 pct Zn couple is necessarily made for the high-Zn side, i.e., near one end of the diffusion-penetration curve where the accuracy is not good. The curves for the Cu/30 pct Zn couple, comparing the present results with the earlier ones

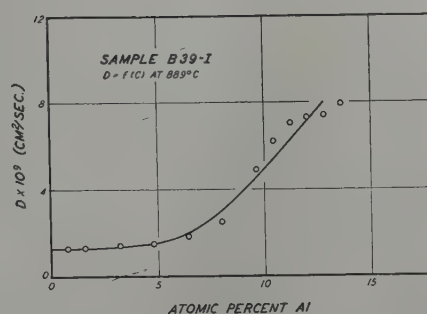


Fig. 32— $D = f(c)$  for sample B39-I.

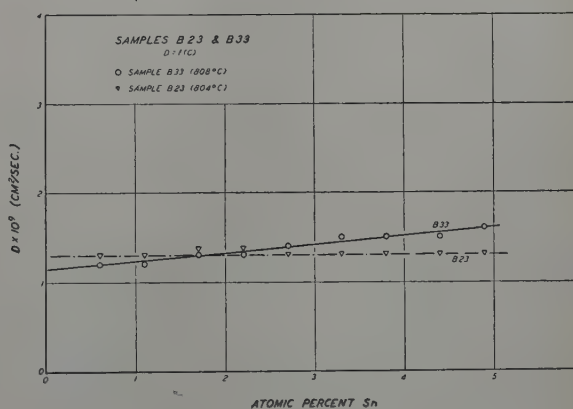


Fig. 33— $D = f(c)$  for samples B23 and B33, Cu/ $\alpha$ Cu-Sn.

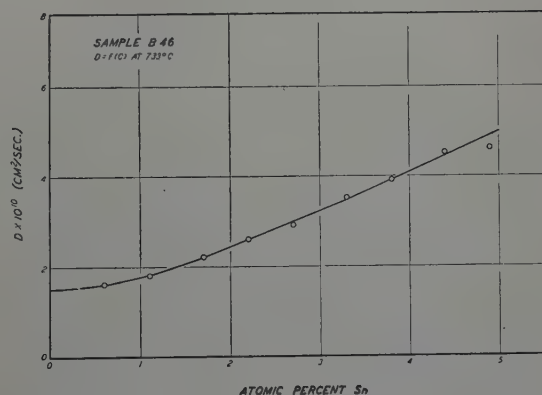


Fig. 34— $D = f(c)$  for sample B46, Cu/ $\alpha$ Cu-Sn.

of Rhines and Mehl show remarkably good agreement.

### Activation Plots

From the preceding data, eq 1 may be plotted for the systems Cu-Zn, Cu-Al, Cu-Sn, and Cu-Ni, Figs. 39 to 42. The activation plot for Cu-Ni, Fig. 42, and the plot of  $Q = f(c)$ , Fig. 45, are surprising; probably further study is needed. The activation plot for Cu-Zn, Fig. 39, shows wide scatter, possibly reflecting appreciable variation in measured  $D$ -values as a result of grain-size differences at low temperatures.<sup>17</sup>

$$Q = f(c)$$

The values of the activation energy  $Q$  as a function of concentration ( $Q = f(c)$ ) may now be plotted, Figs. 43, 44, 45, and 47. These values for the systems Cu-Zn, Cu-Al, and Cu-Sn are in fair agreement with those of Rhines and Mehl;<sup>10</sup> in all cases the direction of change of  $Q$  with increasing concentration is the same. The values of  $Q$  calculated by Rhines and Mehl were known to be highly approximate; these new values are probably better. Fig. 46 plots the frequency factor  $A$  as a function of concentration for the system Cu-Zn.

### Marker Displacement

The methods are given above. The measurements are listed in Table III. The results are plotted in Figs. 48 to 56; in several of these the ordinate is  $t^{1/2}$ , in others the Matano area.

Table III gives the types of markers, the temperature and the time of diffusion, the shift measured, and the method used. Note that several methods are occasionally included in one sample, such as B-45, E-1, etc. Moreover, in some cases markers of different materials were included in one sample, of which sample C-20 is an important example. In this case and in other cases, all markers, whatever their nature, moved by exactly the same amount; the amount of bending of foil markers, whatever their composition, was the same. These materials vary markedly in chemical nature and in physical form and dimension.

Inasmuch as some possibility obtained that marker movement might be related to transport of matter at the interface around an insoluble wire (and therefore be related to diffusion only most indirectly), wire markers were used which dissolved in the matrix; these were of Ni and Pt; Ni dissolved too rapidly; Pt, however, in wire form, 0.001 in. diam, was useful: though it dissolved, the point where it had been (and where the Pt concentration was still high) could be recognized clearly upon etching; this marker moved the same distance as all the others. As noted, the Matano areas, and corresponding marker shifts, are given in Table VI.

Fig. 48 gives the data for the Cu-Zn system at 882°C plotted against  $t^{1/2}$ . As remarked above, data from the direct method are probably most unreliable; these points are represented by open circles, triangles, etc.; the data from the presumably more trustworthy experiments, resulting from application of the other methods ("reference to foils," etc.),

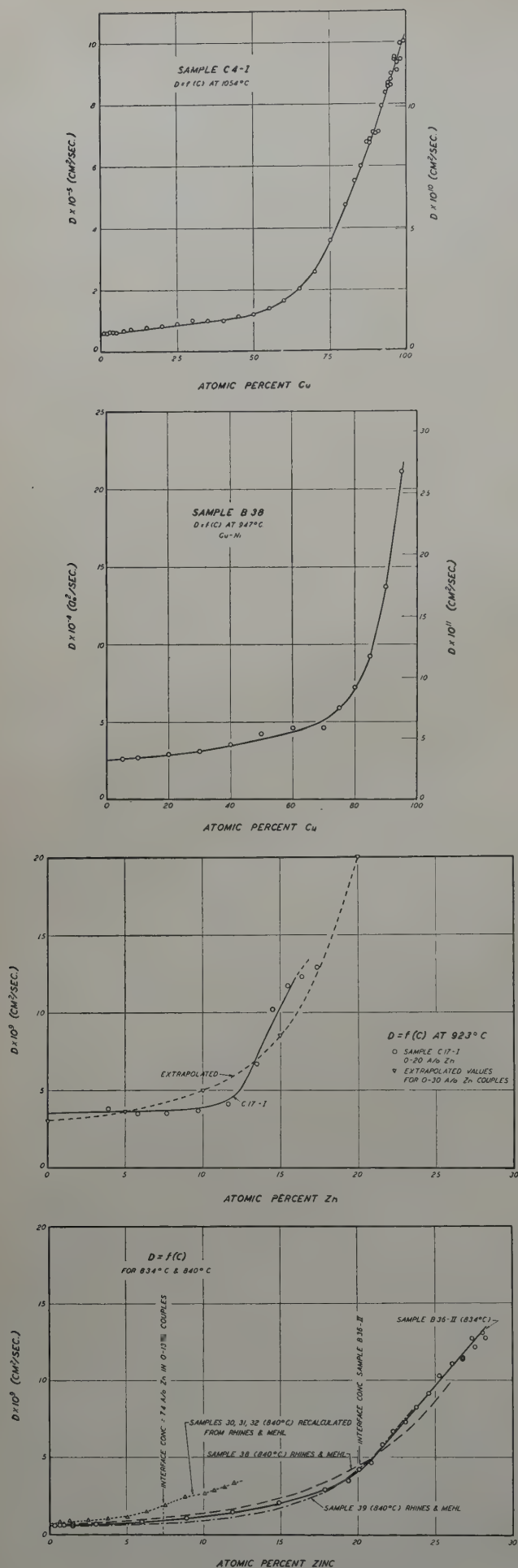


Fig. 35 (top)— $D = f(c)$  for sample C4-I, Cu-Ni.

Fig. 36 (second from top)— $D = f(c)$  for sample B38, Cu-Ni.

Fig. 37 (third from top)— $D = f(c)$  for sample C17-I, Cu/α-brass.

Fig. 38 (bottom)—Comparison of diffusion data for 834° and 840°C, Cu/α-brass.



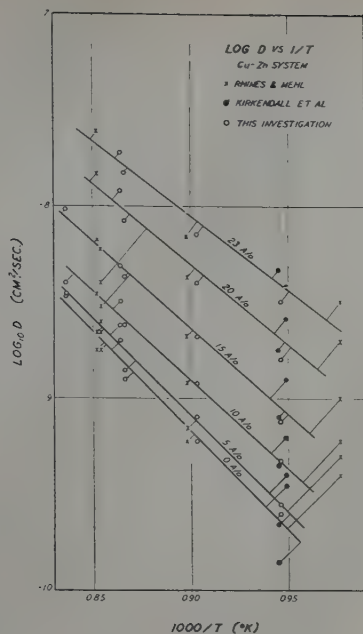


Fig. 39—Log D vs.  $1/T$ , Cu/ $\alpha$ -brass.

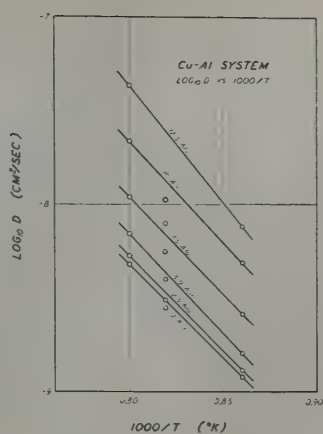


Fig. 40—Log D vs.  $1/T$ ,  
Cu/ $\alpha$ Cu-Al.

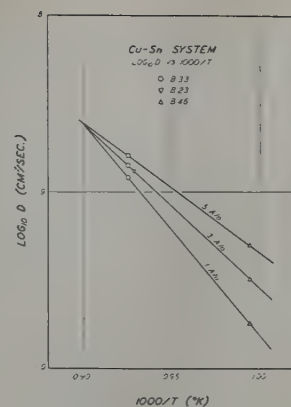
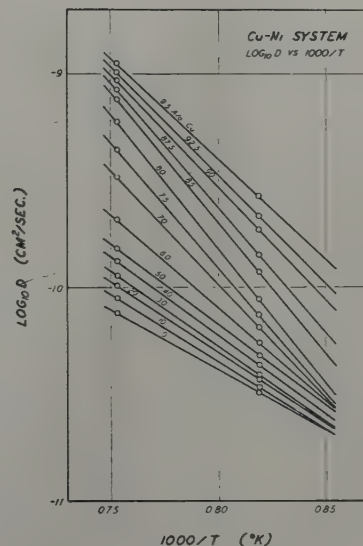
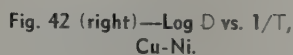


Fig. 41—Log D vs.  $1/T$ ,  
Cu/ $\alpha$ Cu-Sn.



are represented by filled-in points; the curves "observed shift" are drawn from these, ignoring the others. The great scatter shown in the points from the "direct method" is evidence that this method does not yield consistent data and is presumably somewhat unreliable. Using only the filled-in points, the parabolic law is reasonably obeyed. The shift is toward the high-Zn side of the couple (see Figs. 48 to 51) and is nearly the maximum possible shift. Fig. 49, representing data for 834°C, seems to show that the maximum possible shift is nearly attained, though the data are few.

Fig. 50 is a similar plot for a temperature of 784°C; again the shift is near to the maximum possible. The data of Smigelskas and Kirkendall are placed on this diagram; the agreement with the current data is fairly good. The points represented by upright triangles probably should be disregarded, for reasons noted above, and have been disregarded in drawing the curve of observed shift; all points from the direct method have been disregarded. These data include reversed couples, i.e., both Cu/30 pct Zn/Cu couples (as employed by Smigelskas and Kirkendall) and 30 pct Zn/Cu/30 pct Zn couples. No significant difference in the marker shift upon couple reversal is evident.

Fig. 51 combines the data, plotting the Matano area as abscissa. The parabolic law is evident; the current data (here as elsewhere) suggest that the shift is somewhat greater than that measured by Smigelskas and Kirkendall; it shows also that the shift is not far from the maximum possible.

Fig. 52 gives a similar plot for the Cu-Al system. The marker displacement is toward the high-Al side of the couple. It is but a fraction of the maximum possible shift.

The marker displacement in the Cu-Sn system, Fig. 53, is toward the high-Sn side of the couple. Most surprisingly, the shift is greater than the "maximum possible"; the data are few, however, and difficulties in chemical analysis (especially in

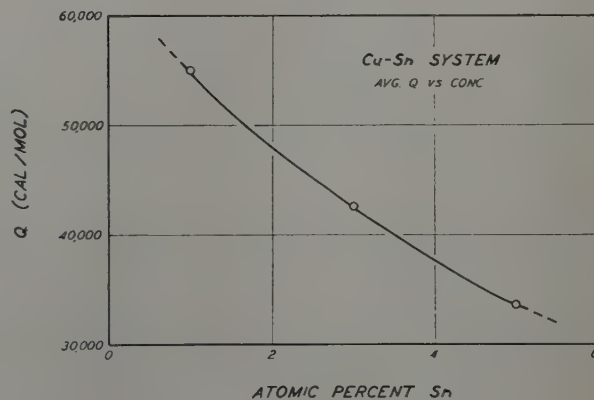


Fig. 43 (second from bottom)— $Q = f(c)$ , Cu/ $\alpha$ Cu-Sn.

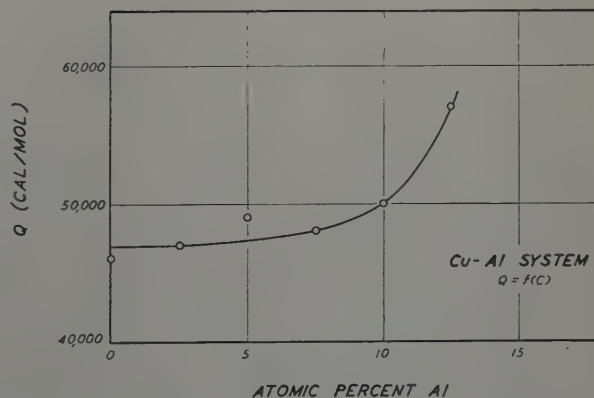


Fig. 44 (bottom)— $Q = f(c)$ , Cu/ $\alpha$ Cu-Al.

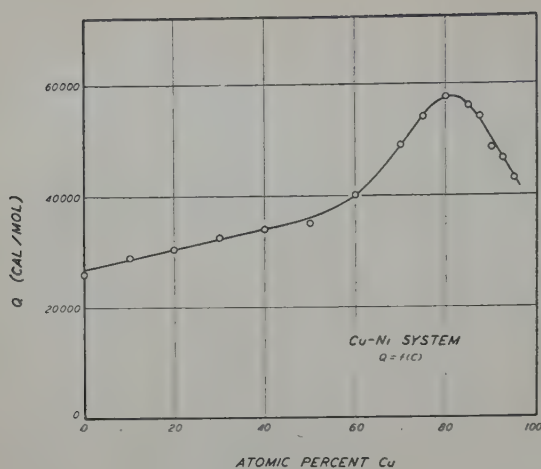


Fig. 45— $Q = f(c)$ , Cu-Ni.

view of the small concentration range involved, viz., 5.5 atomic pct) may render them untrustworthy. The unexpected and even startling nature of these results recommend further study. The results on the systems Cu-Al and Cu-Sn probably suffer from inferior accuracy.

In the Cu-Ni system, the shift is toward the high-Cu side of the couple, Fig. 54. The data are too few to permit a detailed study.

Fig. 55 is an approximation (as noted elsewhere) for the shift in the Ag-Au system, as plotted against (an approximation of) the Matano area. The shift is toward the high-Ag side of the couple.

Fig. 56 is a plot of the shift for the system Cu-Au, plotted against  $t^{1/2}$ . The shift is toward the high-Au side of the couple.

#### Lateral Shift

The method used has been described above; the results are given in Table III, sample C-19. The lateral shift is 0.0007 cm; this is a value for the shift observed in the foils at the interface, corrected for a small shift observed at the other ends of the foils (caused, presumably, by creep, etc.). At the beginning of the diffusion treatment, the composition at the Cu/ $\alpha$ -brass interface was 30 atomic pct Zn; after diffusion this became 21 atomic pct; the lateral shift due to lattice parameter change at this point should be 0.0075 cm, and this should be a decrease in the inter-foil distance at the Cu/ $\alpha$ -brass interface. The observed shift is but one tenth of this. Moreover, if all dimensions of the brass were to decrease by the amount which the ordinary markers shift, i.e., if the shift of the ordinary markers reflects a simple decrease in volume of the brass,

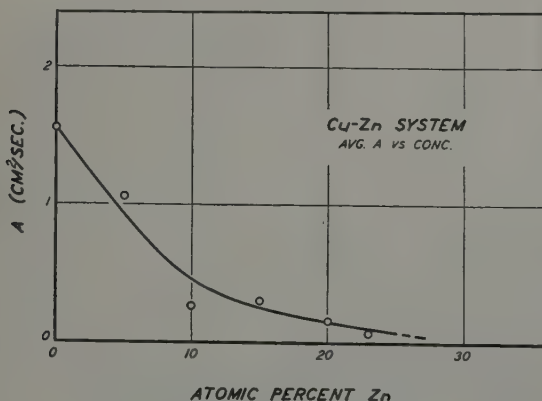


Fig. 46— $A = f(c)$ , Cu/ $\alpha$ -brass.

then a further contraction of 0.0080 cm should occur. These special foil markers thus seem quite inert.

This single observation seems to indicate that dimensional changes are entirely unidirectional—in the direction of the diffusion stream. This validates the common theoretical assumption, though the oddity of the phenomenon would appear to demand further study.

#### Micrographic Studies

Figs. 56 to 58 illustrate the grain structure obtaining at the interface. Apart from deliberately inserted markers, which can readily be seen, some inclusions are visible (on unetched as well as on etched samples, though not easy to show in reproduction); as noted, these inclusions also constitute markers, and move as others do; the micrographs serve also to show the markers in relation to the join.

On the original welded samples, the weld join is, of course, a straight line forming a linear multigrain boundary. This multigrain boundary tends to persist with diffusion, frequently remaining quite straight though sometimes curved; thus grain growth occurs at this point, since the markers move and the grain boundary moves with the markers, during diffusion. It is possible that this is evidence for strain accompanying diffusion, with the generation of imperfections including those of the dislocation type. The long times and the high temperatures of diffusion cause general grain growth; observations of the couples after diffusion are given in Table VII. Much study remains to be done with

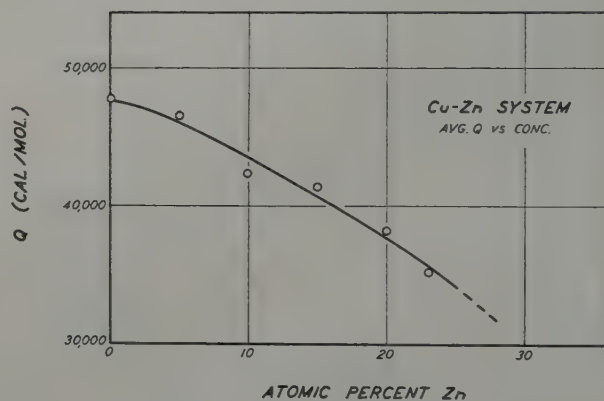


Fig. 47— $Q = f(c)$ , Cu/ $\alpha$ -brass.

respect to grain structure changes during diffusion, and it is more than possible that this will contribute much to the subject and even to the theory of diffusion.<sup>†</sup>

In couples in the Cu-Zn system, some porosity is evident. This porosity (to be distinguished from the very slight traces of "porosity" normally seen in polished sections of alloys, to be ascribed to the embedding of abrasive particles) occurs on the high-Zn side of the couple, Fig. 59. This is the "porosity" observed by Smigelskas and Kirkendall. It is evident, though barely so, in unetched specimens; etching presumably exaggerates it. It does not occur in the high-Cu side of the markers, nor in the immediate neighborhood of the markers, but a very little distance from it. The porosity appears abruptly and is greatest near the marker and decreases in amount with distance from the marker. It occurs only in the diffusion zone—it does not extend beyond it.

<sup>†</sup> These studies are under way, with special emphasis on the use of single crystals and the structural changes that occur in these.



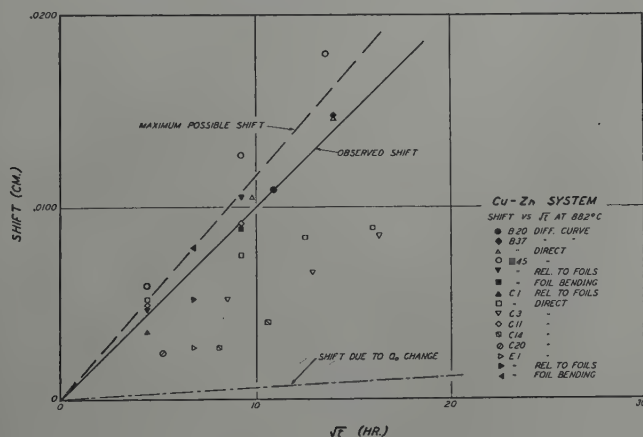
Table VII. Grain Sizes Observed on Couples After Diffusion

| Specimen | Couple                  | Treatment       | Grain Size, mm              |
|----------|-------------------------|-----------------|-----------------------------|
| C-3      | Cu/70Cu-30Zn/Cu         | 267 hr at 883°C | $\alpha$ -brass:1-4; Cu:0.5 |
| C-11     | 70Cu-30 Zn/Cu/70Cu-30Zn | 85 hr at 882°C  | $\alpha$ -brass:2-4; Cu:1-4 |
| C-14     | Cu/70Cu-30Zn/Cu         | 112 hr at 884°C | $\alpha$ -brass:3-8; Cu:1-3 |
| B-22     | Cu/93Cu-7Al/Cu          | 165 hr at 977°C | bronzes:2-4; Cu:3-5         |

Very interestingly, the porosity is evident around the edge of a reference foil, Fig. 4. Despite some effort, this type of porosity was not found in general in the other systems studied, though some slight evidence for it was exhibited in the Cu-Al samples. It suggests, very tentatively, a degeneracy of the structure caused by diffusion.

### Hardness Studies

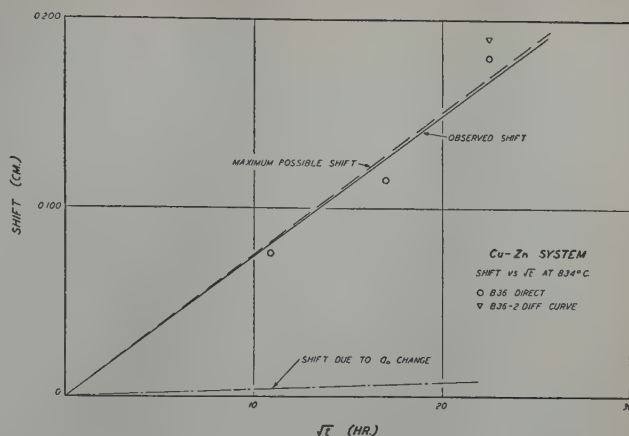
The suggestion that the observed porosity may be evidence of structural degeneracy led to a study of the Knoop microhardness, with 100 g loads (heavier loads did not show the effect) across the diffusion interface. Nine sets were made on the polished sample, normal to the join. Each set consisted in ten measurements, at intervals of 0.0125 cm. These nine sets were arranged so that the different results on different grain orientations would be averaged and this variable eliminated. The total range studied was 0.050 cm, corresponding to a concentration range of 18 to 24 atomic pct Zn. The results are given in Fig. 60. The microhardness of pure Cu was

Fig. 48—Data on marker shift,  $S = K_s t^{1/2}$ , Cu/ $\alpha$ -brass, 822°C.

found to be 95, and that of the 70-30 composition 120; under the conditions of measurement, these values are wholly relative, though proportional to the usual Knoop hardness values. It would be expected that the hardness would change continuously, but the results show a sudden drop on the high-Zn side; this sudden drop appears at about the point where "porosity" becomes evident, and the hardness remains anomalous in the zones of porosity. This is what might be expected in a porous or otherwise degenerate structure. The results previously noted on diffusion-penetration curves, Figs. 37 and 38, might lead to a similar conclusion: that degeneracy obtains in these parts of a couple that lose Zn. This is wholly tentative; further study is certainly required.

### Discussion

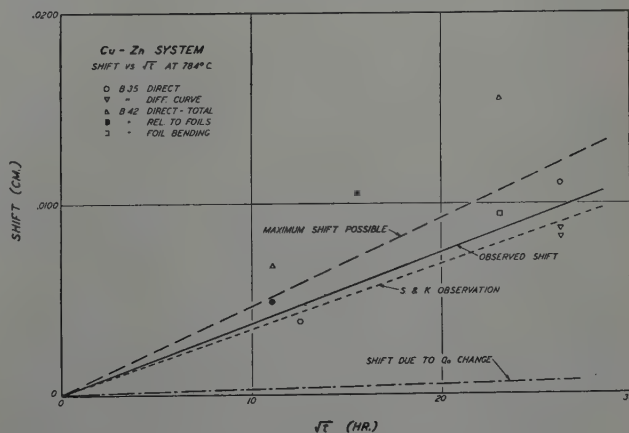
**Phenomenological:** The movement of inert markers in diffusion couples involving a single solid solution is real in the sense that it is a direct concomitant of the diffusion process only and is not an effect originating in nondiffusional processes. The

Fig. 49—Data on marker shift,  $S = K_s t^{1/2}$ , Cu/ $\alpha$ -brass, 834°C.

effect occurs whatever the nature of the marker, and the magnitude of the effect is identical with all markers, even in the case when the marker is not inert but dissolves. Neither the occurrence of the effect nor its magnitude is dependent upon the method of joining the couple (when metallic contact is intimate)—welding and electroplating give nearly the same result. Neither the effect nor its magnitude is dependent upon: (1) The outer geometry of the sample, for the result is the same for couples in which one side is a thin electroplate<sup>1</sup> as for couples in which both parts are heavy blocks, as in the present work; (2) couple reversal, for the marker displacement of a couple of the type A/B/A is identical with that for a reversed couple, B/A/B; (3) differences in the specific reactivities of the surfaces of the component metals with respect to the formation of vacancies, for the surfaces of both parts of the Cu/ $\alpha$ -brass couples were coated with a layer of  $\alpha$ -brass of uniform composition (see discussion below).

The effect occurs in lattice space, and methods are given by which the magnitude of the effect in lattice space may be shown. The effect seems to be unidirectional, occurring only in the direction of diffusion flow, judging from only one—though albeit quite careful—experiment which demonstrated no dimensional change perpendicular to the direction of diffusion flow.

The effect and its magnitude can be affected by secondary factors, such as creep, internal gas generation, and possible recrystallization, but these (except recrystallization) can be experimentally avoided and the basic effect confirmed and accurately measured by newly developed techniques;

Fig. 50—Data on marker shift,  $S = K_s t^{1/2}$ , Cu/ $\alpha$ -brass, 784°C.

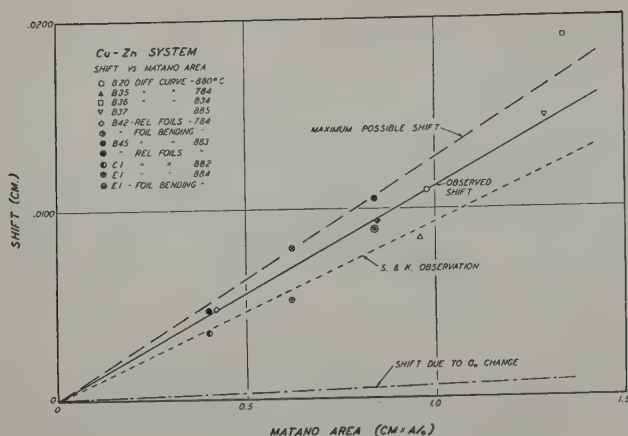


Fig. 51—Data on marker shift, plotted against Matano area, Cu/α-brass.

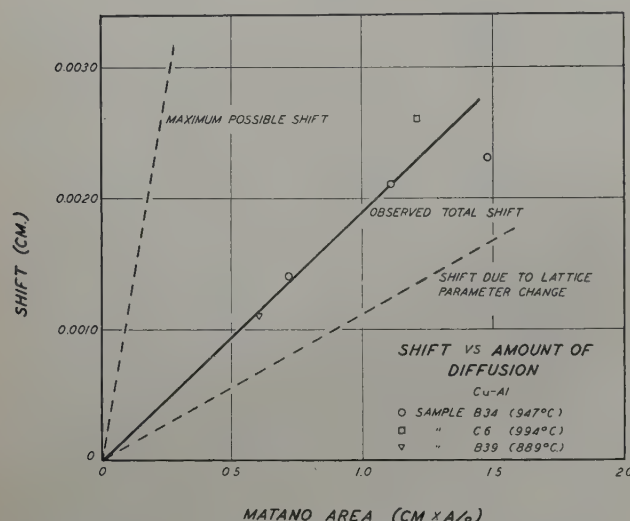


Fig. 52—Data on marker shift, plotted against Matano area, Cu/αCu-Al.

spurious effects are especially pronounced at high temperatures—thus, in Cu/α-brass couples they are negligible at 785° and 834°C, but appreciable at 882°C; the direct method (used by Smigelskas and Kirkendall) gives results which agree with those obtained by better methods of measurement at the two lower temperatures, but not at the high temperature.

The original interface is unambiguously given by the original positions of the unbent portions of the foil markers; the number of atoms on either side is unchanged since there is no diffusion normal to the unbent portions. The bending of the foil edge, as measured from the unbent portion, is thus the shift with respect to the original interface. Inasmuch as all other markers move quantitatively identically with the bending of the foil edge, then all marker shift is referred to the original interface as defined by the unbent foil. Measurements show that the amount of movement is identical with the marker movement referred to the Matano interface. The Matano interface thus defines the original interface. Inasmuch as the whole diffusion area is computed in determining the Matano interface, atoms are conserved on lattice points (else volume increases caused by lattice degeneracy—voids, etc.—would have given a discrepancy between the Matano interface and the original interface). Accordingly, volume anomalies, such as voids (porosity) are too small to be detectable; no change in normal lattice

site vacancies would be expected to give a measurable volume anomaly, for appraisals of the probable fraction of vacant lattice sites show this effect to be beyond these measurements.

**Mechanism:** Smigelskas and Kirkendall proposed that the movement of markers may be taken as evidence that one component of the solid solution diffuses more rapidly than Cu and that the markers move with a bulk movement. All subsequent writers have adopted this point of view. Darken,<sup>4</sup> taking the marker as the origin of a frame of reference for diffusion flow and counterflow, provided a method of calculating the respective dual diffusion coefficients, finding  $D_{Zn} > D_{Cu}$ . Similar calculations can be made for the measurements on the several systems reported herein. (In passing, it should be noted that this in no way invalidates the Matano analysis; this remains a complete quantitative description of c-x diffusion curves.<sup>2</sup>)

Darken's presumption depends upon the somewhat difficult concept of the movement of the "body" of the lattice, which the markers accompany. The validity of this concept, however, appears undoubted in view of the present observation that dissolved Pt markers move as do inert, insoluble markers, for the high-Pt regions are patently integral with the lattice; the much lower magnitude of the diffusion coefficient of Pt renders these regions relatively immobile. (At 800°C the diffusion coefficient of Pt in Cu<sup>12</sup> is one to two hundredth of that of Zn in α-brass.<sup>10</sup>) Radioactive tracers, used recently in this laboratory as markers in the study of multiphase oxidation layers, would doubtless provide similar evidence.

Darken's treatment is purely "phenomenological," i.e., it provided a quantitative treatment of the phenomena but did not contrive a mechanism. Seitz<sup>8</sup> pointed out that diffusion by means of direct atom interchange cannot offer a basis for marker movement, though diffusion through the action of vacancies can, recalling<sup>13</sup> that calculations of diffusional activation energies from first principles for face-centered cubic substitutional solid solutions of a Cu prototype show a preference for diffusion by vacancies over diffusion through interstices, and show that simple two-atom interchange would require prohibitively high energies. Recent calculations by Zener,<sup>14</sup> while altering some numerical values, retain this order of preference; Zener showed on a basis of energetics that a four-atom ring interchange, though requiring more energy than vacancy interchange (though not much) in

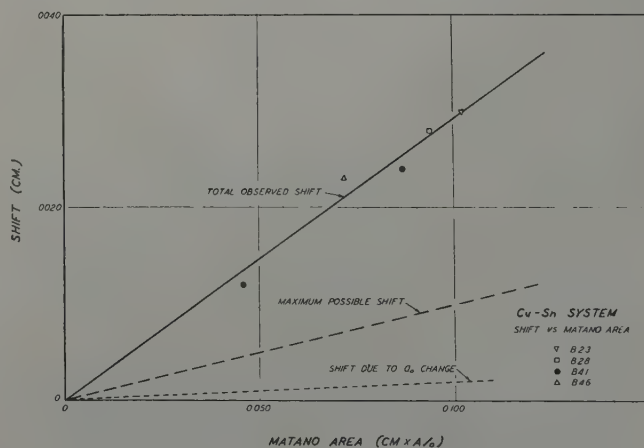


Fig. 53—Data on marker shift, plotted against Matano area, Cu/αCu-Sn.



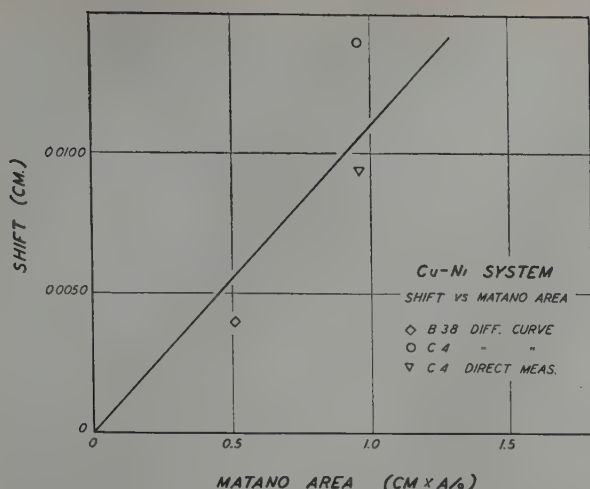


Fig. 54—Data on marker shift, plotted against Matano area, Cu-Ni.

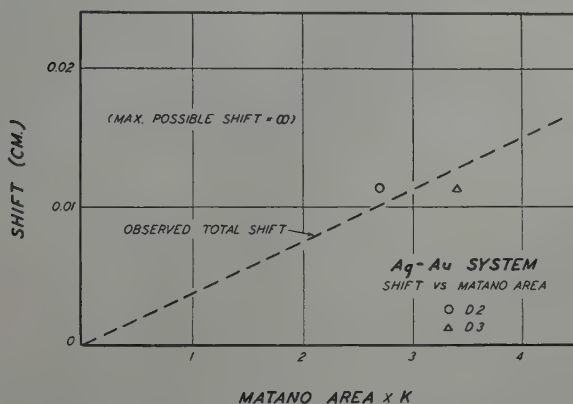


Fig. 55—Data on marker shift, plotted against Matano area, Ag-Au.

face-centered cubic lattices, may be the preferred mechanism in body-centered cubic lattices. Presumably, then, marker movement would not occur in the latter type of lattice (a matter now under study in this laboratory). These calculations are based, to be sure, upon geometrically ideal lattices; whether in real lattices, characterized by subgrain structural units of various types, vacancy diffusion alone obtains, cannot be said. If there be a fine structure to diffusion processes (a possibility deserving attention), with rapid diffusion along the surfaces of imperfection, then a real diffusion process must be represented by a series of fundamental diffusion equations of type 1, each applying to a single structural type of diffusion, as Smekal early proposed,<sup>15</sup> and the atom movement process would be a combination of several types, and, indeed, atom movement mechanisms prohibited in perfect lattices might well occur in the disorder of imperfections.

Seitz,<sup>3</sup> accepting Smigelskas and Kirkendall's idea of mass flow and Darken's analysis, then proposed that the result  $D_{Zn} > D_{Cu}$  means fundamentally that the interchange Zn-vacancy is easier than the interchange Cu-vacancy, so that in the couple Cu/ $\alpha$ -brass vacancies stream predominantly from left to right and Zn atoms from right to left. The accumulation of vacancies to the right was thought to produce voids (manifesting porosity) which in time disappeared by a sintering process, thus providing mass flow; this requires a source of vacancies; he thought the electroplated Cu might be characteristically high in voids and hence vacancies, but conceived the abiding source to be the outer surface of the sample. On this basis, mass flow was held to occur over a

much greater volume than that of the diffusion zone; Darken held it to be restricted to the diffusion zone; Seitz stated that the issue would be resolved by couple reversal, saying that if  $\alpha$ -brass were on the outside of the couple and Cu inside the marker movement would be reversed also. The present work favors Darken on the latter point and greatly limits the possibilities as to the source of vacancies.

The proposal that the stimulating vacancy flow originates at the specimen surface appears quite unlikely: the present experiments show that the marker movement does not vary in any way with the geometry of the sample; couple reversal is without result; the thickness of the Cu portion of the couple is without effect, since nearly the same result was obtained in the present work, where thick Cu disks were used as in Smigelskas and Kirkendall's work, where a thin electroplate was employed. Vacancies in any event could hardly, in the present experiments, have originated in the surface, for the Cu/ $\alpha$ -brass couples were in fact completely covered with  $\alpha$ -brass of the same composition, presumably providing vacancies equally to both elements in the couple, yet the results were nearly the same as those of Smigelskas and Kirkendall where the couple exhibited the surface of only Cu to the ambient. If the porosity observed in the  $\alpha$ -brass portion of the Cu/ $\alpha$ -brass couples is intimately related to mass flow process, then, so far as this portion of the couple is concerned, the effect does not extend throughout the volume of the sample, but is restricted to the diffusion zone.

The vacancy mechanism requires that (1) vacancies be created in the Cu side of the Cu/ $\alpha$ -brass couple, and (2) that (after diffusing) they be destroyed on the  $\alpha$ -brass side. In the light of the present findings, these processes must be limited to the diffusion zone; and in view of the finding that the lateral dimension does not appreciably change, the creation of vacancies in Cu and their diffusion toward and destruction in the  $\alpha$ -brass must remove lattice planes perpendicular to the direction of diffusion in the  $\alpha$ -brass and add perpendicular planes in the Cu.<sup>‡</sup>

The migration of vacancies from the Cu to the  $\alpha$ -brass is not enough to explain mass flow, for it does not in itself explain how lattice planes are added on the Cu side and destroyed on the  $\alpha$ -brass side while maintaining lateral dimensions unchanged. Dislocations might here be advanced as a helpful aid: Fig. 61 illustrates the shrinkage of the  $\alpha$ -brass side of the couple in terms of a simple edge type of dislocation. On this side of the couple,

<sup>‡</sup> For simplicity in discussion the Cu/ $\alpha$ -brass couple will be used as a prototype, with what is said applying also to the other systems studied.

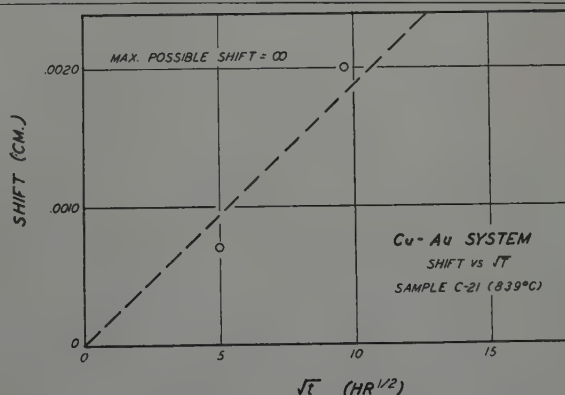


Fig. 56—Data on marker shift,  $S = K_s t^{1/2}$ , Cu-Au, 839°C.





Fig. 57—Micrograph of sample B22, Cu/α-brass,  $K_2Cr_2O_7$  etchant, Cu to left, showing one wire. X100.



Fig. 59—Micrograph of sample B35, Cu/α-brass,  $K_2Cr_2O_7$  etchant, showing one wire. X100



Fig. 58—Micrograph of sample B22, Cu/αCu-Al,  $K_2Cr_2O_7$  etchant, showing one wire. X100.

vacancies presumably could combine, forming a line of vacancies perpendicular to the direction of diffusion flow; this combination could then shrink to a dislocation of the type shown in Fig. 61 IV. This effectively destroys a lattice plane, giving marker movement as pictured, and maintains the constancy of lateral dimensions. Any three-dimensional void would provide three-dimensional contraction, and dislocations oriented otherwise than pictured would do likewise. Presumably it is the elastic restraint of the couple as a whole that restricts contraction to

the plane perpendicular to direction of diffusion flow.

Inasmuch as there is reason to believe that even annealed metals exhibit a characteristic concentration of dislocations, Zn atoms wandering toward the Cu, there find dislocations awaiting, and by a simple reversal of the process shown in Fig. 61, destroy a dislocation by occupying positions between dislocation edges, thus ultimately creating a new lattice plane.<sup>§</sup> This is a simple scheme offering possibilities of elaboration.\*\*

This mechanism meets the requirements: lattice planes are destroyed on the α-brass side and created on the Cu side. The interaction of vacancies and dislocations is fundamental. It is probably oversimple to think of the two processes of destruction and creation as restricted respectively to the extremes of the diffusion zone; they would probably overlap within that zone. The creation of voids or porosity is not necessary, and indeed voids are not found in some systems studied herein, as noted above; whether or not voids form probably relates to the ease with which dislocations may form.

The marker shift varies greatly from system to system. In the Cu-Zn, Cu-Al, Cu-Sn systems the markers moved away from the Cu side of the couple; in the Cu-Ni system, toward the Cu side; in the Ag-Au system, toward the Ag side; in the Cu-Au system, toward the Au side. The magnitude of the marker shift varies greatly: it is relatively great in the Cu-Zn, Cu-Ni, and Ag-Au systems, and relatively small in the Cu-Al and Cu-Sn systems. As Darken's analysis<sup>4</sup> shows, these movements can be referred to the respective values of two diffusion coefficients for each system. And in turn this implies a greater rate of interchange with vacancies

<sup>§</sup> In those systems in which there is a marked change in lattice dimensions with concentration, stresses may well arise causing plastic flow and resultant recrystallization and grain growth, multiplying the dislocation concentration and facilitating the process pictured; there is ample evidence that recrystallization, or at least grain boundary movement, does occur in diffusion in α-brass.<sup>17</sup>

\*\* Having seen this proposal, Seitz<sup>18</sup> has further developed it, employing dislocations of the ring type.



of the atom with the greater separate diffusion coefficient. No *a priori* way of predicting this is available.

If one assumes that diffusion is by the vacancy mechanism, with maintenance of equilibrium or near equilibrium of vacancy concentration, and with no sensible voids created, then self-diffusion measurements in alloys might possibly be taken to predict the direction of movement of markers; from Johnson's results on self-diffusion coefficients in a 50:50 atomic pct Ag-Au alloy,<sup>18</sup> it would then be predicted that the marker would move toward the silver side of the couples, which indeed it is observed to do in the experimental work given above. Whether self-diffusion coefficients in the pure components could be used somewhat similarly cannot be said, for such coefficients are either not available, or too uncertain in accuracy, or not applicable (as in the case of Zn, where the data apply to hexagonal Zn, not to the cubic lattice concerned).

### Summary

This is an experimental study of the movement of markers during diffusion in solid solutions, the phenomenon discovered by Kirkendall. Six systems have been investigated, at a series of temperatures: Cu/ $\alpha$ -brass; Cu/Sn $\alpha$ -solid solution; Cu/Al  $\alpha$ -solid solution; Cu/Ni; Ag/Au; Cu/Au; diffusion couples have been made by welding. Markers of many types have been used, including W, Mo, Ni, Pt wires; Pt, Ta, Fe, Ni foils; C, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> powders. All markers move, and by the same amount in a given system, the phenomenon is thus not a property of the marker; the movement, with respect to the Matano interface, has been measured for the separate systems. In the Cu/ $\alpha$ -brass couples, the markers move toward the high-Zn side; in the Cu-Al system, toward the high-Al side; in the Cu-Sn system, toward the high-Sn side; in the Cu-Ni system, toward the Cu; in the Ag-Au system, toward the Ag; in the Cu-Au system, toward the Au. Measurements agree reasonably well with Kirkendall's, showing that the technique of joining is unimportant. The Matano interface agrees with the original interface, showing conservation of atoms on lattice sites, and showing porosity to be negligible.

The amount of marker shift differs from system to system, for unexplained reasons; the amount of shift is sometimes near the maximum possible; it is large in Cu-Zn and Cu-Ni systems, smaller in others. Dimensional changes seem to be restricted to the direction parallel to diffusion flow. Cu/ $\alpha$ -brass couples exhibit apparent traces of porosity in the diffusion zone (and anomalously low hardness there), while no such porosity could be found in other systems. Only the vacancy mechanism of

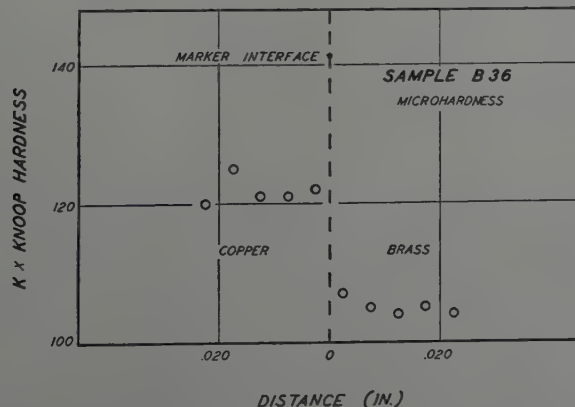


Fig. 60—Microhardness traverse on sample B36, after diffusion, Cu/ $\alpha$ -brass.

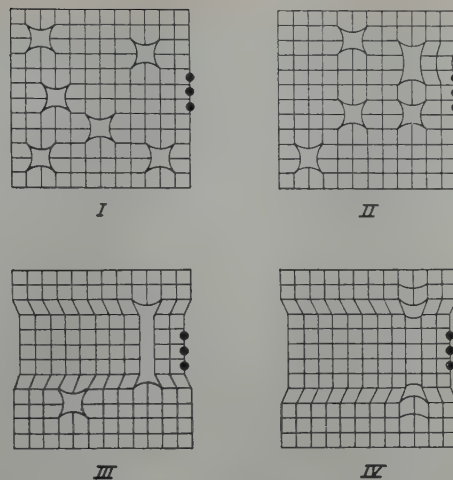


Fig. 61—Vacancies (I), coagulating to voids (II and III), resulting in dislocations (IV), and resultant mass flow and marker (small dot) displacement.

diffusion appears to be useful in explaining these phenomena, though several theoretical points remain to be explored. Inasmuch as the amount of shift is independent of the nature of the external surface of the diffusion couple, and of the dimensions of the couple, it appears that operating vacancies cannot come from external surfaces but must be generated within the diffusion zone itself. A dislocation mechanism is proposed to explain marker shift.

### Acknowledgment

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# Effect of Ternary Additions on the Age-Hardening Of a Copper-Silver Alloy

by Harold Margolin and Walter R. Hibbard, Jr.

The effect of ten ternary additions on the aging of a Cu-Ag alloy was measured by X ray, microstructure and hardness. A super-saturated copper-rich transition structure was found. The effect of the ternary element was related to differences between transition and precipitate lattice parameters and analogies with solution and strain hardening.

IN addition to the prerequisite of diminishing solid solubility with falling temperature, the theory of coherency hardening<sup>1</sup> proposes that the principal source of hardening during precipitation is strain caused by coherency between the matrix and precipitate. For a given system greater coherency hardening would result from lengthening the period of coherent growth and/or increasing the number of nuclei, other things remaining equal. However, the hardness change during aging is a function of a number of phenomena in addition to coherency hardening, such as dispersion hardening, loss of coherency, solute depletion, matrix recovery or recrystallization, coalescence, and their relative time sequences.

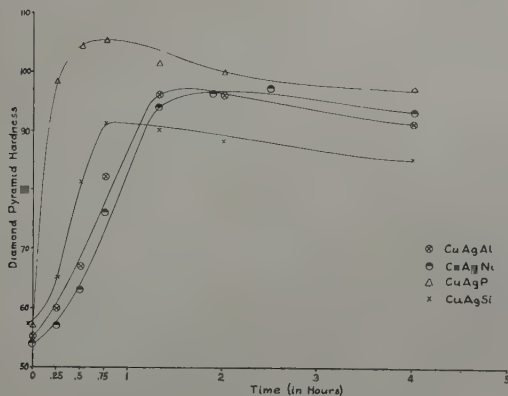


Fig. 1—Aging curves for 500°C.

The present investigation was undertaken to study the effect of ternary additions on the age-hardening of Cu-Ag alloy. For this purpose a series of alloys were made containing as ternary constituents Mg, Al, Si, P, Mn, Ni, Zn, As, In, and Sb. These elements were added to a master 5 wt pct Ag in Cu alloy in

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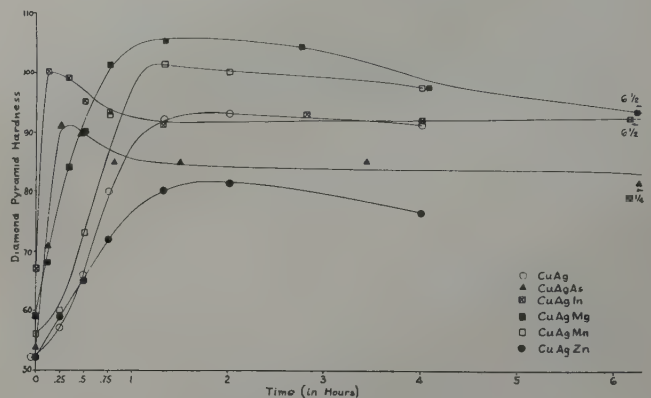


Fig. 2—Aging curves for 500°C.

such amounts as to obtain alloys listed in Table II containing the following approximate atomic percentages: 96 pct Cu, 3 pct Ag, 1 pct ternary addition. A 97 atomic pct Cu, 3 atomic pct Ag alloy was used as a comparison standard.

There have been numerous investigations of age-hardening in Cu-Ag alloys<sup>2-10</sup> but few of ternary Cu-Ag alloys. Pfister and Weist<sup>11</sup> found that 1 wt pct Ni reduced the solubility of Ag in Cu above 600°C and that the rate of precipitation was slower than in polycrystalline Cu-Ag alloys of similar silver content. More recently Hodge, Jaffee, Dunleavy, and Ogden<sup>12</sup> investigated the effect of ternary additions of Mg, Li, P, Cd, Zn, Zr and Be on strength properties of Cu-Ag alloys. Mg, Cd, and P were found to increase strength in the aged and cold-worked condition.

## Experimental Procedure

Charges weighing 7.5 lb were melted in a closed carbon crucible under a reducing atmosphere\* of nitrogen and hydrogen. A Durville-type casting procedure with a hot-top arrangement was used to obtain a sound casting, 2x2x4<sup>3</sup>/<sub>4</sub> in. Prior to rolling and annealing of the ingots, a trial solution anneal of rolled sections of the hot-top portions indicated that at 780°C melting was avoided except for the Cu-Ag-Sb alloy. This alloy could not be produced as a single phase within the limits of temperature control,  $\pm 3^\circ$  to  $5^\circ$ C, since melting occurred at 640°C, and below this temperature precipitation was

\* This gas, a nonexplosive reducing mixture containing 93 pct N<sub>2</sub> and 7 pct H<sub>2</sub>, dried by passing through H<sub>2</sub>SO<sub>4</sub>, was also used in all annealing and aging treatments.



Table I. Lattice Parameters for Various Alloys

| Alloy     | Cu, A  | Ag, A | Cu Transition, A | Aging Time at 550°C, Hr |
|-----------|--------|-------|------------------|-------------------------|
| Cu-Ag     | 3.6137 | 4.069 | 3.658            | 90                      |
| Cu-Ag-Al  | 3.6130 | 4.068 | 3.657            | 24                      |
| Cu-Ag-Sb  | 3.6194 | 4.065 | 3.668            | 24                      |
| Cu-Ag-In  | 3.6151 | 4.103 | 3.710            | 24                      |
| Cu-Ag-Mg  | 3.6132 | 4.068 | 3.670            | 29.5                    |
| Cu-Ag-Mn* | 3.6130 | 4.074 | 3.656            | 29.5                    |
| Cu-Ag-Ni  | 3.6114 | 4.073 | 3.653            | 29.5                    |
| Cu-Ag-P   | 3.6129 | 4.066 | 3.655            | 24                      |
| Cu-Ag-Sb  | 3.6236 | 4.082 | 3.662            | 44                      |
| Cu-Ag-Si  | 3.6131 | 4.068 | 3.654            | 44                      |
| Cu-Ag-Zn  | 3.6142 | 4.072 | 3.648            | 24                      |

\* In addition to the silver and transition copper lines, other unidentified lines were seen.

found. Prior to the final solution treatment the alloy was not heated above 630°C.

Specimens for hardness tests were produced by step-wise cold rolling and annealing longitudinally split sections of the casting, approximately 1 in. thick, to a common thickness of 0.165 in. and thence in two reductions of 30 pct each to a final thickness of 0.080 in. Wire specimens for lattice parameter measurements, prepared by a schedule similar to that for hardness specimens, were 0.077 to 0.080 in. in diam. These wires were not etched. Both hardness and lattice parameter specimens were in the cold-worked state prior to the final solution treatment.

With the exception of Cu-Ag-Mg, which was annealed at 800°C, and Cu-Ag-Sb, which was annealed at 650° to 675°C, the alloy specimens 1x $\frac{3}{8}$ x 0.080 in. were solution-annealed from 24 to 48 hr at 775°C and quenched in water.

A Rockwell hardness tester, fitted with a 136° diamond pyramid penetrator and a total load of 27.6 kg was employed to obtain the diamond pyramid hardness values.

Debye-Sherrer X-ray patterns were obtained with copper radiation, monochromated by reflection from a cleavage section of penta-erythritol. Exposures of one to three days were required, and, because of the large grain sizes, rotation of the specimens did not always eliminate spottiness. Lattice parameters based on the 420  $K\alpha_1$  and  $K\alpha_2$  and the 331  $K\alpha_1$  and  $K\alpha_2$  for the stable copper solid solution were determined by Cohen's method<sup>18</sup> of extrapolation and checked against a  $\cos^2\theta$  extrapolation. Parameters determined by these methods checked within 0.0003A. The errors

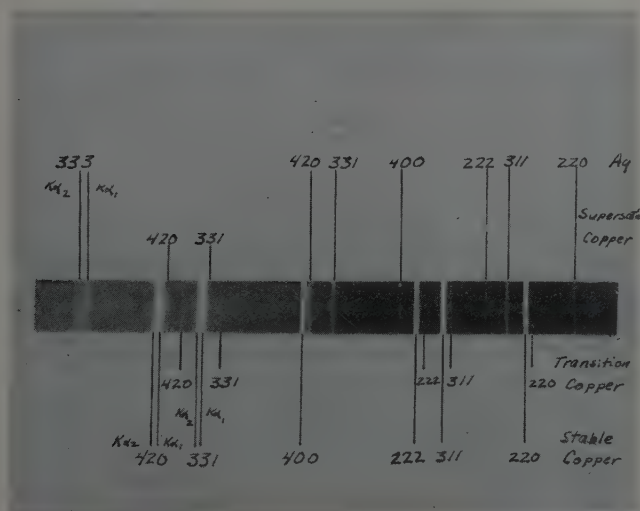


Fig. 3—Debye-Sherrer pattern of Cu-Ag-Al aged 24 hr at 550°C.



Fig. 4 (top)—Cu-Ag solution treated 120 hr at 775°C and quenched.

Fig. 5 (bottom)—Same as Fig. 4 but aged 20 hr at 550°C.

in the transition copper parameters based on the 420  $K\alpha_1$  and 331  $K\alpha_1$  lines and the silver parameters determined from the 333 reflections are estimated to be  $\pm 0.0025$  and  $\pm 0.002A$ , respectively.

### Evaluation of Quenching Conditions

The as-quenched hardness of the alloys varied considerably from 52 for Cu-Ag to 69 for Cu-Ag-In. Hardness tests and microscopic examination of three specimens selected at random from a group of 24, which had simultaneously been solution annealed and quenched, and three specimens individually suspended but otherwise given the same treatment, indicated that the quenching conditions were constant within the errors of hardness measurement and random selection of specimens.

### Hardness Deviations

In general each hardness value was obtained by averaging the hardness of three specimens upon which four impressions each had been made, a total of 12 values. The as-quenched hardness values varied very little. However, in some aged specimens deviations occurred up to 33 DPH points, which exceeded the maximum measurement error of  $\pm 2$  DPH points.

An analysis of the hardness data revealed no correlation with grain size or temperature of treatment. However, the deviations in intermediate (Cu-Ag-Ni) and high (Cu-Ag-P and Cu-Ag-Mg) hardness alloys were greater than those in the low hardness alloys (Cu-Ag-Si and Cu-Ag-Zn). This suggests that hardening did not take place uniformly in all ternary Cu-Ag alloys exhibiting high hardness and having intermediate to large grain size.

### Experimental Data

Aging treatments were carried out at 350°, 400°, 450°, and 500°C. Typical hardness vs. time curves obtained for aging at 500°C are shown in Figs. 1 and 2. Debye-Sherrer patterns were obtained from specimens overaged at 550°C for periods of 24 to 90 hr. Films, shown in Fig. 3, of all overaged alloys revealed three sets of lines, two of which were clearly identifiable as (a) intense Cu solid solution lines and (b) broad less intense Ag solid solution lines. The third fainter set of lines was displaced from the intense Cu rings, so as to correspond to reflections from a greatly expanded and probably transitional copper-type lattice. Calculations of lattice parameters on this basis are given in Table I. Lines due to the unstable, supersaturated Cu solid solution appeared for all alloys after aging at 550°C, even after 90 hr at temperature for binary Cu-Ag.

To determine the source of the expanded copper lattice, X-ray exposures were made of Cu-Ag in the solution annealed and in the aged conditions. The pattern obtained after a 120 hr solution anneal and quench, shown in Fig. 4, disclosed only sharp copper lines. After this specimen was given a 20 hr overaging treatment at 550°C, transition copper and

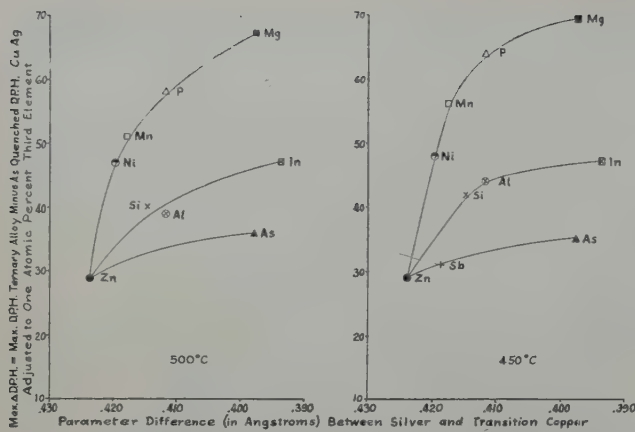


Fig. 6 (left)—Effect of lattice parameter difference on the adjusted age-hardening increment for 500°C.

Fig. 7 (right)—Same as Fig. 6 for 450°C.

silver lines appeared in addition to the stable copper solid solution lines, see Fig. 5. Thus the expanded lattice producing the transition copper lines is formed during aging, probably the result of segregation of silver beyond the equilibrium solubility limits, which would be a logical step in the formation of silver precipitate and the transition phase.

### Distribution of the Third Element

With the exception of the lattice expansion found in Cu-Ag-In and Cu-Ag-Sb, the silver precipitate parameters show changes which lie within the limits of error of measurement. However, this is in contrast to the transition copper lattice parameters, which experience the greatest changes, and the stable copper solid solution matrix lattice parameters. There appears to be no general correlation between expansion or contraction of the transition lattice parameters and those of the copper matrix or between the variations of copper matrix and silver lattice parameters. The changes in parameter of the silver and transition copper in the ternary alloys are unpredictably greater or less than the change in the Cu-Ag alloy, indicating that the third element does not always act to cause closer matching between the silver and transition copper phases which are assumed to be coherent during the early stages of growth of the silver precipitate.

Where the third element does not affect silver lattice parameters, but is probably present in the transition and/or the stable copper solid solution,

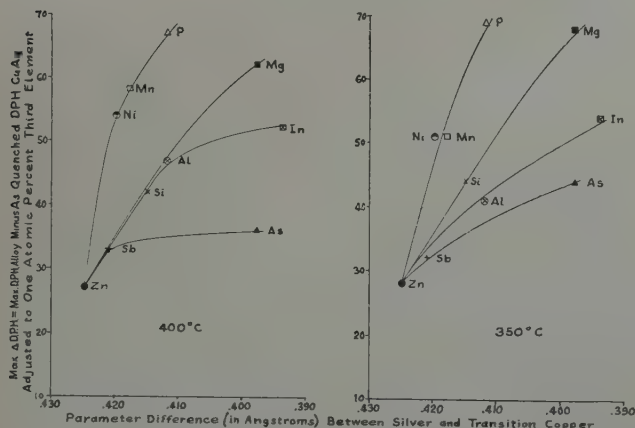


Fig. 8 (left)—Same as Fig. 6 for 400°C.

Fig. 9 (right)—Same as Fig. 6 for 350°C.

changes in their lattice parameters may be the result of a redistribution of the third element after silver has precipitated. Variations in the transition copper lattice may be caused, in the case of expansion, by local concentration of the third element. A contraction of this lattice, however, may result from diminished solubility of silver in the transition structure.

### Maximum Hardness

Since the precipitation mechanism of this series of alloys is similar, it would appear that the maximum hardness values should be related to the degree of matching or difference between the lattice parameter of the silver and the transition copper phases. Since the recrystallization phenomenon is less significant at higher aging temperatures,<sup>10, 14</sup> this relationship would be more distinguishable for the data at these temperatures. Plots of maximum hardness at 450° and 500°C vs. parameter difference indicate that as the sizes of the two lattices converge the hardening increases.

These plots, however, do not take into account small differences in solution hardening nor the variations in the exact atomic composition, see Table II. Therefore, if the difference between the maximum hardness attained by a ternary alloy at any particular aging temperature and the as-quenched Cu-Ag hardness is considered as a measure of the hardness increment added to the basic alloy by the third element, this increment ( $\Delta H$ ) can be extrapolated or interpolated to exactly 1 pct, as necessary.

Table II. Atomic and Weight Percentages of Alloys

| Alloy     | Ag, Wt Pct | 3rd Element, Wt Pct | Ag, Atomic Pct | 3rd Element, Atomic Pct |
|-----------|------------|---------------------|----------------|-------------------------|
| Cu-Ag     | 4.95       |                     | 2.98           |                         |
| Cu-Ag-Al  | 4.88       | 0.48                | 2.92           | 1.14                    |
| Cu-Ag-As  | 4.88       | 1.025               | 2.94           | 0.89                    |
| Cu-Ag-In  | 4.75       | 1.84                | 2.88           | 1.05                    |
| Cu-Ag-Mg  | 4.79       | 0.31                | 2.87           | 0.82                    |
| Cu-Ag-Mn  | 4.83       | 0.84                | 2.90           | 0.99                    |
| Cu-Ag-Ni* | 4.52       | 0.94                | 2.71           | 1.04                    |
| Cu-Ag-P   | 4.76       | 0.45                | 2.85           | 0.94                    |
| Cu-Ag-Sb  | 4.78       | 1.47                | 2.89           | 0.79                    |
| Cu-Ag-Si  | 4.88       | 0.43                | 2.92           | 0.99                    |
| Cu-Ag-Zn  | 4.87       | 0.075               | 2.93           | 0.97                    |

\* The analysis of all alloys except Cu-Ag-Ni was performed by Lucius Pitkin, Inc., New York.

Figs. 6, 7, 8, and 9 show the adjusted values of  $\Delta H$  for the temperatures of aging employed. It can be seen, first, that as the differences between the silver and the transition copper lattices decrease, the hardness increases; second, that several rates of hardness changes are evident; and, third, that these relationships exist for all aging temperatures investigated. Thus, there is good general agreement with predicted behavior, although certain detailed differences in hardness change cannot be correlated with individual parameter difference (e.g., Cu-Ag-Al, Cu-Ag-Si, and Cu-Ag-P) or with periodic sequence of the ternary elements. The hardness values for Cu-Ag-In and Cu-Ag-Sb essentially represent measurements of recrystallized material, since in both cases almost complete recrystallization takes place before the hardness maximum is attained. A comparison of hardness values for certain alloys at 450°C indicated that, depending on the alloy and, possibly, the time of aging, the nonrecrystallized areas were as hard and sometimes harder by from 10 to 20 DPH points as the corresponding recrystallized areas. Guy, Barrett and Mehl<sup>15</sup> have shown that a separate, more rapid rate of hardness change exists for the recrystallized areas in Cu-Be alloys.



The ternary solute elements, arranged in decreasing order of the maximum hardness increment, are P and Mg, Mn, Ni, In, Al, Si, As, Sb, and Zn. Hodge et al.<sup>12</sup> have also found that phosphorus and magnesium strengthen Cu-Ag but find "very little effect on the tensile strength" when 1 to 3 wt pct Zn is added to a 6 pct Cu-Ag alloy.

### Rate of Hardening

Examination of the hardness-time curves indicated that certain alloys consistently hardened more rapidly than others. A correlation similar to that for  $\Delta H$  was found for the time to attain one half maximum hardness and the difference between the lattice parameters of silver and transition copper phases. If, at any particular temperature, the difference between the time for each ternary alloy and the basic Cu-Ag alloy to attain one half maximum hardness is adjusted for exactly 1 atomic pct third element, and these adjusted values are plotted against the difference between the silver and transition copper lattice parameters similar figures also are obtained as shown in Figs. 10, 11, 12, and 13.

It will be seen that in general the data for each temperature are scattered along two straight lines which are included to indicate qualitative trends. With the exception of Cu-Ag-P and Cu-Ag-Mg those alloys hardening most rapidly have the lower ad-

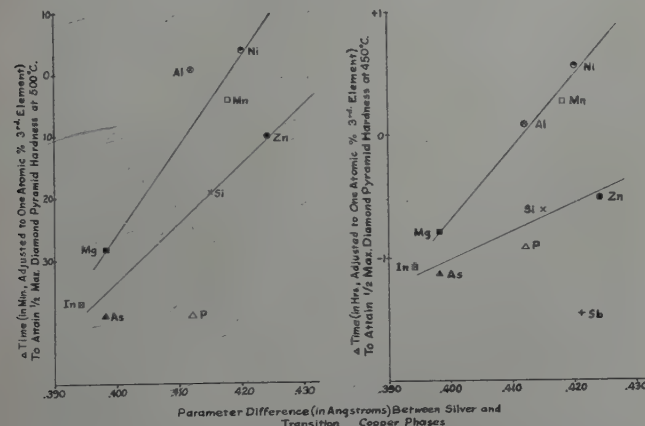


Fig. 10 (left)—Effect of lattice parameter difference on the adjusted time increment for half hardening at 500°C.

Fig. 11 (right)—Same as Fig. 10 for 450°C.

justed maximum hardness increment values. It may be noted that, as the parameter difference increases, the rate of hardening decreases. Moreover, those elements which, when dissolved in copper distort its lattice the least, are generally at the low hardening rate end of their respective lines. This suggests that the rate of age hardening may follow a pattern similar to the rate of strain hardening experienced by binary copper, solid solution alloys. Some data on binary copper alloys are available from Martin,<sup>18</sup> in which the hardness of alloys after constant reduction is plotted against the atomic percent of solute. For the Cu-Ag base alloys, the hardness difference between the unworked alloys and those given 20 and 60 pct reduction have been adjusted to exactly 1 atomic pct solute, and plotted against the parameter difference between silver and transition copper phases. The resulting graphs are shown in Figs. 14 and 15. With the exception of magnesium there is good agreement between Martin's data and the authors', suggesting that the third element dissolved in the transition phase and/or the matrix during coherent growth of the precipitate has a similar

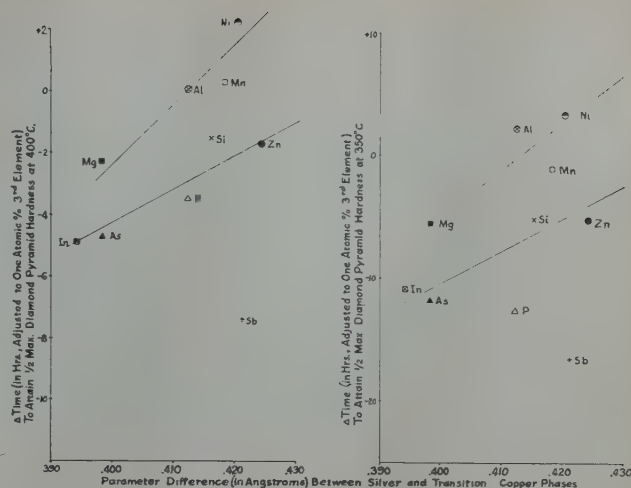


Fig. 12 (left)—Same as Fig. 10 for 400°C.

Fig. 13 (right)—Same as Fig. 10 for 350°C.

effect on coherency hardening as it does on work hardening, i.e., more rapid coherency and work hardening occur with increased lattice distortion. Since the rate of recrystallization is slow in Cu-Ag-P, the high rate of hardening may possibly be the result of a high rate of nucleation and possibly by more extended coherent growth.

The elements, arranged in decreasing order of their influence on the rate of hardening are Sb, As, In, Mg, Si, Zn, Al or Mn, and Ni.

### Microstructure

Examination of specimens mechanically polished and etched with copper-ammonium-chloride was principally confined to hardness specimens aged at 450° and 500°C and lattice parameter specimens aged at 550°C. The observed phenomena may be classified in the sequence in which they occur, (a) precipitation within the grain, (b) grain boundary reaction, and (c) coarsening of precipitate.

**Precipitation Within the Grain:** The procedure employed in obtaining hardness-time curves was to use individual specimens for several different accumulative isothermal aging times at a given temperature. Accelerated precipitation occurred in slipped regions around hardness impressions. Fig. 16 shows one of these areas in a specimen of Cu-Ag-P aged

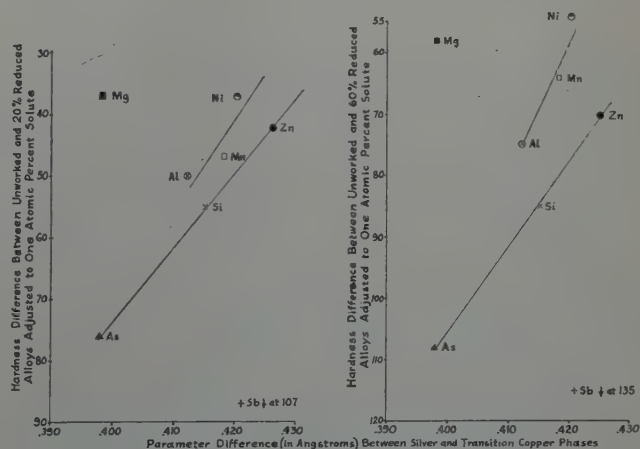


Fig. 14 (left)—Effect of lattice parameter difference on the adjusted work-hardening increment for 20 pct reduction.

Fig. 15 (right)—Effect of lattice parameter difference on the adjusted work-hardening increment for 60 pct reduction.

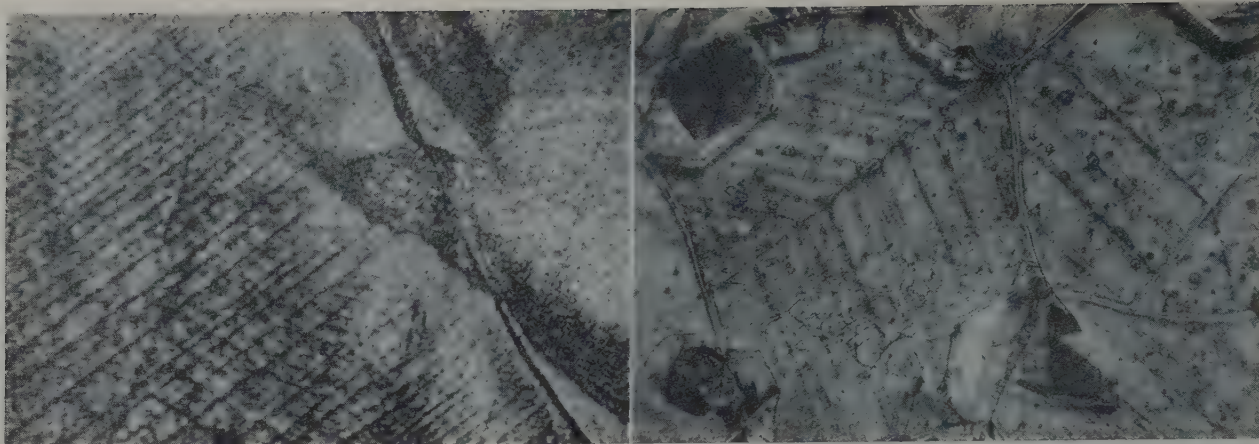


Fig. 16 (left)—Cu-Ag-P aged  $1\frac{3}{4}$  hr at  $450^{\circ}\text{C}$ . Area of photograph near hardness impression. Copper-ammonium-chloride etch. X800.  
Fig. 17 (right)—Cu-Ag-Mn aged  $1\frac{1}{2}$  hr at  $448^{\circ}\text{C}$ . Copper-ammonium-chloride etch. X200.

Former slip planes along which precipitation has taken place. These planes traverse intragrain boundaries without deviation.

approximately to maximum hardness after  $1\frac{3}{4}$  hr at  $450^{\circ}\text{C}$ .

Fig. 17 shows a type of structure which at  $450^{\circ}\text{C}$  is common to all alloys except Cu-Ag-P, Cu-Ag-As, Cu-Ag-In, and Cu-Ag-Sb. The interior of grains are subdivided by irregular boundaries. It was suspected at first that these boundaries might be a freak etching effect. A specimen of Cu-Ag-Al was polished and etched with copper-ammonium-chloride, and these lines were developed. The specimen, repolished and etched with ammonium persulphate, did not reveal these boundaries. However, when the as-ammonium-persulphate-etched specimen was re-etched with the first etchant the sub-boundaries, together with the precipitation associated with hardness impressions, reappeared.

These lines are similar in appearance to grain boundaries. Both regions are bordered by a light etching area which suggests that silver, at least, must diffuse from these light etching regions to the boundaries in order to precipitate. The internal boundaries differ from grain boundaries in that the recrystallization phenomenon rarely begins in these areas, although it is often seen at grain boundaries. The two also differ in that the subboundaries enclose regions differing slightly in orientation, as shown by Fig. 17.

It is possible that the internal boundaries were formed prior to aging and that precipitation in these boundaries reveals them. Wood and Rachinger<sup>17</sup> working with aluminum found similar structures which were best revealed by slow deformation at high temperatures, conditions which did not apply in the present study. Intra-grain boundaries readily seen as comparatively short aging times were less distinguished in some specimens of the same alloy aged longer times at  $450^{\circ}\text{C}$ . The internal subdivisions are not at all evident in lattice parameter specimens aged at  $550^{\circ}\text{C}$ . Possibly an explanation of this phenomenon may require consideration of a time-temperature-supersaturation relationship.

A Widmanstätten structure was found in all alloys, but for Cu-Ag-In, Cu-Ag-Sb, Cu-Ag-As, and Cu-Ag-P only in the lattice parameter specimens aged at  $550^{\circ}\text{C}$ . The structure of Cu-Ag-P was most difficult to resolve, a fact which suggests that the high hardness of this alloy may be due to a high rate of nucleation. A Widmanstätten structure was seen before maximum hardness in several instances (Cu-Ag, Cu-Ag-Mg, Cu-Ag-Si, and Cu-Ag-Zn) and

most likely represents localized overaging. No attempt was made to identify the planes of precipitation, but where the precipitate was clearly resolvable no more than three directions of plates were seen.

**Grain Boundary Reaction:** The grain boundary or recrystallization reaction occurred early in the precipitation process and was found to diminish in amount as the aging temperature increased. At high magnifications or where the precipitate was coarse, the recrystallized regions showed a pearlitic-like arrangement of phases.

The procedure of aging and hardness testing adopted afforded some opportunity to observe the effect of cold work on the recrystallization reaction. Generally more recrystallization was revealed near and within the hardness impressions, although the extent varied from alloy to alloy. Fig. 18 shows a region near a hardness impression in which recrystallization has begun, but the direction of most rapid growth is not along the most severely deformed directions. On the other hand, Fig. 16 reveals an instance where growth proceeds along deformation lines in regions of high energy. Therefore, it appears likely that there is an orientation as well as energy dependency for this type of recrystallization.

It was observed frequently during use of the Tukon microhardness tester that slip lines (emanating from hardness impressions) within a given grain changed direction upon entering the recrystallized areas associated with this grain. In some regions traversing slip lines disclosed twins, as shown in Fig. 19.

**Coarsening of Precipitate:** During growth of the recrystallized grains at  $450^{\circ}\text{C}$  the silver particles within them grew resolvable and the spacing between the particles increased. The transition was quite gradual and no boundaries between the two regions could be seen. However, in Cu-Ag alloys aged  $9\frac{1}{2}$  hr at  $450^{\circ}\text{C}$  the coarsening of silver commenced at the recrystallized grain boundaries, as shown in Fig. 20; and in Cu-Ag-In, also aged  $9\frac{1}{2}$  hr at  $450^{\circ}\text{C}$ , at the original grain boundaries as well, although the specimen is almost entirely recrystallized. At 1500X, as shown in Fig. 21, it can be seen that the new precipitate tends to form perpendicular to the advancing interface as in growing pearlite nodules.<sup>18</sup> Some lattice parameter specimens, aged at  $550^{\circ}\text{C}$ , particularly Cu-Ag, also revealed the



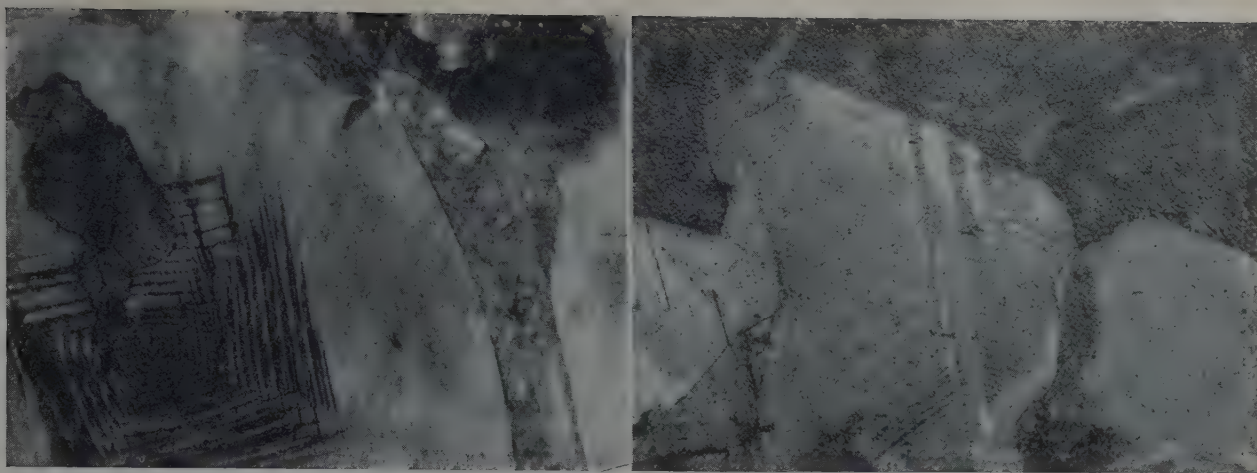


Fig. 18 (left)—Cu-Ag-P previously hardness tested and aged  $1\frac{3}{4}$  hr at  $450^{\circ}\text{C}$ . Copper-ammonium-chloride etch. X100.  
Recrystallization at hardness impression.

Fig. 19 (right)—Cu-Ag aged  $3\frac{1}{2}$  hr at  $450^{\circ}\text{C}$ . Copper-ammonium-chloride etch. X500.  
Twins outlined by slip lines in recrystallized grains.

coarsening phenomenon. At  $450^{\circ}\text{C}$  the coarsening reaction occurred primarily at the original grain-recrystallized grain interface, whereas the reaction in the parameter specimens took place primarily at recrystallized boundaries. The general characteristics of the coarsening phenomenon at the recrystallized grain boundaries suggest that a second re-orientation of the precipitate may be taking place.

### The Precipitation Reaction

Precipitation in Cu-Ag and ternary Cu-Ag alloys appears to include the following phenomena:

1. Segregation of silver (and third element where involved) beyond equilibrium solubility limits† in the case of Cu-Ag, and probably in the ternary alloys as well, to form a transition copper-base structure rich in silver
2. Limited coherent growth of the precipitate, involving coherency possibly between precipitate and transition copper lattice and coherency between transition copper and the matrix copper lattice poorer in silver
3. Breaking away of the precipitate, recrystallization, and coarsening

It is entirely possible that the silver precipitate during its coherent growth may exist in a transition form, the entire mechanism thus being similar to that described by Geisler and Newkirk<sup>20</sup> for per-

manent magnet alloys. However, no evidence was found relating to a transition silver-base lattice.

The existence of the transition lattice for extended periods of time at relatively high temperatures may be rationalized on the basis of the experimental fact that large Widmanstätten plates form before maximum hardness is attained. This suggests that coherency does not extend for long times, since loss of coherency and growth of the precipitate in some areas must occur quite rapidly, even before the coherent precipitate is formed in other areas. In view of the sluggishness of the diffusion of silver in copper and the reduction of supersaturation during precipitation, a marked reduction in rate of precipitation during its latter stages might be expected. Evidence of an expanded copper phase on films of all specimens aged at  $550^{\circ}\text{C}$  lends support to this suggestion. Another possible reason for the existence of transition copper lines is connected with the occurrence in certain alloys of the second recrystallization or coarsening phenomenon which must involve resolution and reprecipitation of the silver phase.

† Minimum size of transition copper lattice was measured at  $3.648\text{\AA}$  (Cu-Ag-Zn), and for the transition phase of Cu-Ag the parameters were measured as  $3.658\text{\AA}$ . The lattice parameter of copper containing the maximum equilibrium content of 4.87 atomic pct Ag<sup>10</sup> is  $3.633\text{\AA}$ . Based on the assumption that Vegard's law holds in this enforced solid solution, the silver contents of the transition phases of Cu-Ag-Zn and Cu-Ag are approximately 8 and 10 atomic pct, respectively.

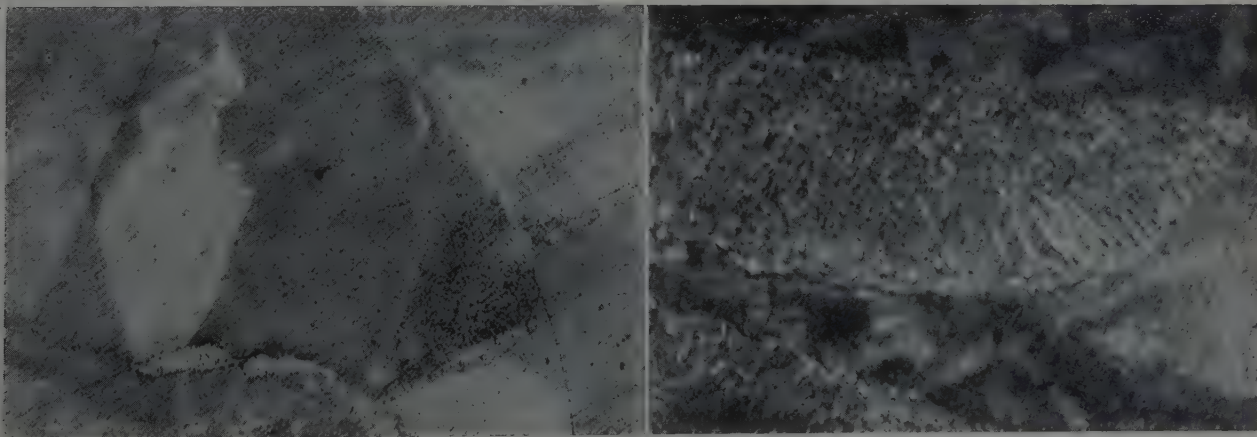


Fig. 20 (left)—Cu-Ag aged  $9\frac{1}{2}$  hr at  $450^{\circ}\text{C}$ . Copper-ammonium-chloride etch. X500.  
Coarsening phenomenon beginning at recrystallized grain boundaries.

Fig. 21 (right)—Cu-Ag-In lattice parameter specimen aged 24 hr at  $550^{\circ}\text{C}$ . Copper-ammonium-chloride etch. X1500.  
Coarsening reaction. (Oblique illumination)



The recrystallization phenomenon appears to be associated with internal stress, for this process occurs most readily in areas immediately surrounding hardness impressions and at low temperatures where hardness and related internal stresses are greatest. When aging temperatures are raised, the extent of recrystallization diminishes and in Cu-Ni-Co<sup>20</sup> and Cu-Ag<sup>21</sup> alloys the phenomenon can be completely suppressed by slow cooling. In experiments on Cu-Be tri-crystals, Guy, Barrett, and Mehl<sup>16</sup> have shown that during aging at 200° and 300°C cracking occurs along grain boundaries where the recrystallization reaction has occurred. No further grain boundary precipitation took place after the formation of cracks, and if aging was carried out at 400°C, no cracking occurred.

Jones, Leech and Sykes<sup>10</sup> have suggested that recrystallization, i.e., discontinuous precipitation, takes place when the temperature is low and the supersaturation high, and that continuous precipitation is prevalent at high temperatures when supersaturation is low. The necessary definitive experiment, i.e., aging alloys of the same constituents but of different compositions at temperatures where the respective degree of supersaturation is the same, has not been performed. Indeed, considerable information is lacking as regards the observed coarsening reaction, subsequent to recrystallization. A program of study involving microstructure examination of large grained specimens during aging and possibly orientation relationships between recrystallized and unaltered areas<sup>22</sup> would probably disclose useful information concerning both phenomena.

### Summary

1. A transition copper-base structure, quite rich in silver, has been found during aging in all the investigated alloys, which are Cu-Ag, Cu-Ag-Al, Cu-Ag-As, Cu-Ag-In, Cu-Ag-Mg, Cu-Ag-Mn, Cu-Ag-Ni, Cu-Ag-P, Cu-Ag-Sb, Cu-Ag-Si, and Cu-Ag-Zn.

2. The ternary elements do not generally appear to be distributed in such a manner as to bring about a closer matching between the silver precipitate and the transition copper lattices. The lattice parameters of the transition phases are most affected by the presence of the third element, whereas with exceptions of Cu-Ag-As, Cu-Ag-In, Cu-Ag-N, and Cu-Ag-Sb the parameters of the copper solid solution and the silver precipitate are relatively unchanged.

3. In general, the maximum increment of hardness, adjusted to exactly 1 atomic pct third element, increases with diminishing difference of the silver and transition copper lattice parameters.

4. Rates of hardening, adjusted for exactly 1 atomic pct third element, generally show an increase with decreasing difference between the silver and transition copper parameters. Those ternary elements, which cause the greatest solution hardening in binary copper alloys, effect the most rapid response to coherency and strain hardening.

5. Microstructure examination has revealed precipitate in Widmanstätten form, along intra-granular boundaries, and in recrystallized nodules prior to attainment of maximum hardness. The intra-granular boundaries differ from grain boundaries in that the former do not appear to enclose regions differing widely in orientation and do not serve as sites at which recrystallization begins. It is also seen that the recrystallization phenomenon, commencing almost completely at grain boundaries, is followed by a coarsening reaction, which is seen at the inter-

faces between recrystallized and nonrecrystallized grains and at recrystallized grain boundaries.

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# El Paso Refinery Of Phelps Dodge Refining Corporation

by B. B. Kunkle

The history of this refinery has been one of expansion. It now has the capacity to produce 240,000 tons of cathodes annually. A general flowsheet and descriptions of the plant layout, operations involved, and equipment used at one of the world's largest and most modern electrolytic copper refineries are presented.

THE El Paso copper refinery of Phelps Dodge Refining Corp. was originally constructed by the Nichols Copper Co., in association with Phelps Dodge Corp. and the Calumet & Arizona Mining Co., in order to refine anode copper produced at the smelters of the two latter companies.

Initial production was obtained from the plant in January 1930 and its annual refining capacity was 100,000 tons of anodes.

In order to keep pace with Phelps Dodge Corp.'s increasing copper production in the Southwest, it became necessary in 1937 to increase the El Paso plant's refining capacity to 160,000 tons of cathodes annually. This was accomplished by adding two sections to the electrolytic tank house, increasing the number of anodes placed in each commercial electrolytic tank from 33 to 37, and making changes in the dc circuits which made it possible to put three generators on each of the two circuits instead of two, thus increasing the amperage on each circuit from 10,000 to 14,800 amp. The capacity of the two furnaces from which refined shapes were cast was increased by raising the sidedoor bays on the furnaces 6 in.

An increase of 70 pct in the productive capacity of Phelps Dodge Corp.'s Morenci Branch in 1942 again made it necessary to expand refining capacity. In order to accomplish this, Defense Plant Corp. set up a project to increase the capacity of the El Paso plant to 240,000 tons of cathodes annually. This project consisted of enlarging the tank house approximately 50 pct, the construction of another wire-

bar furnace, and corresponding increases in other departments where necessary. The engineering work on this expansion was begun in March 1942. Actual construction was under way by August 1942, and the work was completed by March 1944. These additional facilities were purchased from Defense Plant Corp. by Phelps Dodge Refining Corp. in August 1949.

The plant is in El Paso about eight miles east of the center of the city and near Highway 80 and the main lines of the Southern Pacific and Texas & New Orleans railroads. The plant site covers approximately 494 acres of company-owned land that is ideally adapted for its use, being well-drained sandy soil and having enough slope so that a minimum amount of excavation was required when the plant was constructed. There is still ample room on the plant site for any future plant expansion.

The plant is constructed on four different ground levels and so arranged that the unrefined copper is unloaded on the highest level at the north side of the plant and the refined copper is shipped out from the lowest level on the south side of the plant. The receiving or unloading platform, weighing and sampling rooms, main floor of the tank house, acid and condensate storage tanks, and the slimes and copper sulphate plants are on the first or highest level. The tank house basement, yard scales, charging and furnace bays, balloon flue and stack, brick-storage building, substation and power house, boiler feedwater treating plant and pump house, water storage tanks, and change houses are on the second level. This second level also contains ample yard area for setting-up furnace charges, and for storage of custom scrap, cathodes, scrap anodes, blister, coke, and poles. The casting wheels, inspection conveyors, cathode shears, wire-bar scalping machine, slag

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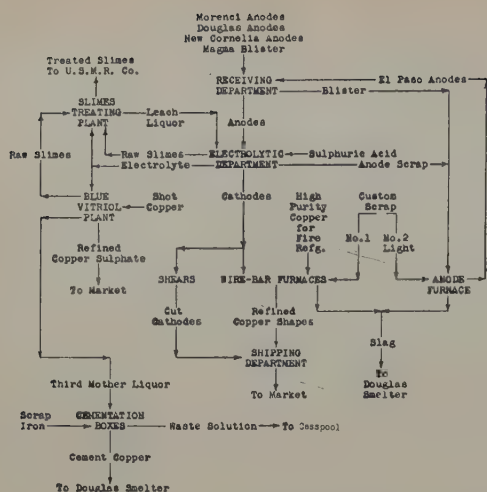


Fig. 1—Flowsheet of El Paso Refinery.

dump, and shipping department are on the third level. There is also a storage area on this third level, adjacent to the casting building, for storing moulds and refined shapes. The warehouse, machine shop, laboratories, engineering and administrative offices, personnel offices, first-aid station, water-cooling ponds and pump house, and parking lots for the employees are on the fourth or lowest level.

Transportation of materials into and out of the plant, except for the small amount trucked in, is by means of a main spur from the Southern Pacific railroad and six side spurs to various parts of the plant. Transportation of copper between the various departments in the plant is by means of a 30-in. gage track system using locomotives powered with electric motors or combustion engines. A general flow-sheet of the plant is shown in Fig. 1.

### Receiving and Sampling

The copper refined at the plant consists of anode copper produced at Phelps Dodge Corp.'s three smelters in Arizona, blister copper produced at Magma Copper Co.'s smelter in Arizona, and No. 1, No. 2, and Light custom scrap copper received from dealers throughout the western part of the United States.

All anode and blister copper is unloaded, weighed, and sampled by the receiving department. This copper is delivered to the plant in or on standard gage box or flat cars, these cars being spotted on a spur adjacent to and paralleling the receiving platform. The receiving platform, adjacent to the north side of the tank house, is approximately 662 ft long and 91 ft wide, and is paved with concrete. This area provides ample space for the six unloading stands, two 20-ton track scales, drilling and sampling rooms, and storage for anodes.

The anodes are unloaded, by means of hand trucks and air hoists, from the railroad cars into anode rack cars that hold the same number of anodes that are loaded into a commercial electrolytic tank. After the anodes are loaded into the anode rack cars, the net weight of the copper in each one is determined carefully. The cars containing the anodes that are not sampled are taken directly into the tank house for unloading into the electrolytic tanks, or unloaded and placed in stock according to requirements. The

cars containing the anodes that are to be sampled are stored on tracks east of the drilling room in an area provided for that purpose. After these anodes have been drilled, they are handled in the same manner as the others.

Blister copper is unloaded by stacking it on the floor of the anode rack cars, about 50 pieces in each car. After weighing and sampling, this copper is delivered to the yard for unloading into storage or transferring to cathode flat cars for charging to the anode furnace.

The drilling room is equipped with air hoists for handling the copper and three drilling units. A separate room is provided for grinding, screening, quartering, and otherwise preparing the samples for the laboratory. All drilling is done according to carefully designed templates.

### Custom Scrap

Custom scrap is received in a yard area east of the receiving department and is serviced by a standard gage railroad siding that also serves the blue vitriol plant. The copper scrap is unloaded on an area, 40x250 ft, paralleling the tracks and paved with reinforced concrete. An unpaved area to the east provides space for burning insulated wire.

After unloading, the copper scrap is sorted and classified according to the best established refinery practice. Only No. 1, No. 2, and Light copper is accepted. It is then sampled, baled, and weighed. No. 1 copper is charged to the wire-bar furnaces, and No. 2 and Light copper is charged to the anode furnace.

### Electrolysis

The multiple-system tank house consists of one large room that has an east-west length of 775 ft and a north-south width of 328 ft, thus covering an area of nearly 6 acres. The building has red hollow-tile walls and a cast-gypsum roof, the top of the roof being protected with Barrett specification roofing. The walls and floor of the basement, as well as the main working floor, are concrete. The building has three monitors in the roof which extend the entire length of the building. The center monitor has 25 Robertson ventilators which provide natural ventilation. Large, continuous windows in both the walls and monitors provide ample natural light during the day. Hinged sections in these windows provide a means for greater ventilation during the summer months. The maximum, inside height of the monitors above the working floor is approximately 41 ft. The electrolytic tanks are separate from the working floor, and both are supported by concrete columns in the basement. The clearance between the basement floor and the working floor is approximately 7 ft.

There is one central pump bay 36 ft wide extending the entire length of the tank house. This bay has a maximum depth of approximately 15 ft below the level of the working floor and contains the sumps, pumps, head tanks, storage tanks, and other equipment required to handle the electrolyte and slimes.

There are two crane bays on each side of and parallel to the pump bay. Each of these four crane bays, which contain the electrolytic tanks, are 73 ft wide and are equipped with a total of seven overhead, two-hook cranes; namely, two 15-ton Shaw-Box cranes and five 12½-ton Milwaukee cranes. A No. 14 Bedford transfer crane, at the east end of the tank house, is provided for transferring cranes from



one crane bay to another. These cranes are used for placing anodes into and removing anode scrap and cathodes from the electrolytic tanks, stripping operations, and handling starting-sheets and suspension bars.

The electrolytic tanks are constructed of reinforced concrete 5 in. thick, adjacent tanks having a common wall, and they are lined with 8-lb, 6 pct antimonial lead. The inside dimensions of each tank, after the lead lining is in place, is about 13 ft 2¼ in. long, 43 in. wide, and 46 in. deep. Thirty-two, 2-in. fiber-conduit weep holes are spaced equally in the bottom of each tank so that leaks in the lead lining can be detected quickly. The tanks are supported by reinforced concrete columns capped with 1-in. thick glass plates.

There are 38 sections of 32 tanks each and 17 sections of 36 tanks each, making a total of 55 sections and 1828 electrolytic tanks. Normally, 52 sections having a total of 1728 tanks are used for producing commercial cathode copper, and 3 sections having a total of 100 tanks are used for producing starting-sheets. The 32 tank sections have two rows of 16 tanks each and the 36 tank sections have two rows of 18 tanks each. The commercial electrolytic tanks have a capacity of 37 anodes and 38 cathodes, the spacing between anodes is 4 in. The starting-sheet electrolytic tanks have a capacity of 34 anodes and 33 starting-sheet blanks, the spacing between anodes is 4½ in.

The Whitehead single-contact system is used and a Baltimore groove is cast in the top of the positive lug of each anode. Three electrical circuits are used: No. 1 consisting of 2 starting-sheet sections and 18 commercial sections, No. 2 consisting of 18 commercial sections, and No. 3 consisting of 1 starting-sheet section and 16 commercial sections. The average maximum current density used on each of the three circuits is about 20.5 amp per sq ft. The average voltage measured across each commercial section is about 6 v.

The electrolyte is separated into five separate circulations or liquor circuits. Two of these liquor circuits have 16 commercial sections on each of them, while the other three have 8 commercial, 8 commercial and 1 stripper, and 4 commercial and 2 stripper sections on them, respectively. A total of 15 Worthington centrifugal pumps are provided for pumping the electrolyte. Eight of these pumps are used normally for circulation purposes, three are standby pumps, and four are used for pumping into or out of storage tanks. Ten of the pumps are the vertical type and the balance are the horizontal type. The circulation of the electrolyte through the electrolytic tanks is from bottom to top in a longitudinal direction at an average rate of 4 to 5 gpm.

Seven, single-pass floating-head Karbate heaters made by the Chemical Equipment Manufacturing Co. have been installed recently to heat the electrolyte, the electrolyte passing through these heaters while it is being pumped from the sumps to the head tanks. These heaters consist of a bundle of tubes made of Karbate through which the electrolyte passes, the tubes are enclosed in a lead-lined steel shell into which steam is injected. The 1-in. diam lead-pipe coils in the sumps, formerly used for heating the electrolyte, are now used only for standby and occasionally auxiliary heating purposes. The temperature of the electrolyte in the head tanks is maintained at approximately 145°F.

The addition reagents added to the electrolyte

consist of glue and sodium chloride. Excess copper is removed from the electrolyte by means of electrolytic tanks in the commercial sections loaded with insoluble lead instead of copper anodes. The free sulphuric acid content of the electrolyte is maintained by the additions of 66 Bé H<sub>2</sub>SO<sub>4</sub> and distilled water. The amount of impurities in the electrolyte are controlled by withdrawing solution from the liquor circuits and sending it to the blue vitriol plant where it is used for making commercial grades of copper sulphate.

The electrolyte contains an average of about 3.5 pct Cu, 17.5 pct free H<sub>2</sub>SO<sub>4</sub>, and 0.0025 pct Cl. Sufficient addition reagents are added to the electrolyte to produce a smooth cathode that is not too hard.

The commercial anodes have a body 36 in. sq and weigh approximately 690 lb. Stripper anodes, cast in the El Paso refinery, have a body 38 in. wide and 37½ in. high, and weigh approximately 840 lb. Starting-sheets are 37½ in. sq and the average weight is about 11½ to 12 lb without the loop.

The average anode cycle is about 26 days. The average commercial cathode cycle is about 13 days. Starting-sheets are stripped daily.

Normally, the commercial sections are operated with one side charged with new anodes and the other side charged with half-run anodes. Thus, the anode scrap must be removed from one side of the section, the slimes cleaned out of the tanks, and new anodes loaded into them each time the cathodes are pulled from both sides. Anode scrap is pulled from one side of each stripper section every two weeks.

Starting-sheets are looped with a single loop 18 in. wide, threaded with a suspension bar, and placed in racks in the same areas where the stripping is done. The racks of starting-sheets then are placed on top of the sections where they are required. The sheets are flapped dry on stainless steel flapping boards and placed in the tanks by hand after the anodes are in place. This is the only flapping that is done. Metermen and hot-sheet men work daily on top of the sections eliminating the short circuits that occur between the anodes and cathodes.

Four cathode washing machines, two on each side of the pump bay, are in the basement. The cathodes are loaded into these washers with the cranes through openings in the working floor. Chain conveyors carry the cathodes in a vertical position through these washers while hot distilled water under high pressure is sprayed on them. When the cathodes are discharged from the washers, they fall in a flat position on cathode flat cars and are ready to be hauled to the yard for weighing.

Openings in the working floor also are provided for loading anode scrap, after it has been washed free of slimes, upon cathode flat cars in the basement so that it can be removed to the yard for weighing.

The tank house slimes, which contain the precious metals and other insoluble anode impurities, are collected in a separate launder system when they are cleaned from the electrolytic tanks. After screening through a 35-mesh screen, these slimes are pumped in the form of a slurry to storage tanks in the basement of the slimes treating plant.

### Slimes Treating Plant

The building is 100 ft east of the tank house and consists of a 19x54-ft main building with four floors and a basement and a 38x39-ft south extension with a main floor and basement, the basements are on the same level as the tank house basement. The walls



are made of red hollow tile. The main building has air-tight windows made of glass blocks, the inside walls have a smooth coating of plaster, and the reinforced concrete floors are all sloped and provided with drains so they can be washed.

The main building is ventilated with a large blower. The suction of this blower is connected to pipes that extend to and have one or more openings on each floor. Dampers are located near each opening so that flow of air into them can be regulated. Air is drawn into the building on each floor through adjustable louvers in the walls. The air from the blower is discharged into a scrubber where any dust that may be in the air is removed with water before it is discharged to the outside. This method of ventilation prevents the loss of any dust.

Copper is present in the tank house slimes in the form of metallic copper and copper selenide and telluride. The purpose of the slimes treating plant is to reduce the copper content of the slimes to 3.0 pct or less. This is accomplished by aeration in tank house electrolyte.

The slimes slurry pumped from the tank house to the three storage tanks in the basement is allowed to settle. The clear liquor is returned to the tank house and the thickened slurry is pumped to tanks on the top floor of the building where further thickening is accomplished by settling and decantation. The resulting heavy slimes slurry is charged to four leaching tanks, on the same floor, that previously have been charged with tank house electrolyte. These lead-lined wooden tanks are about 6½ ft sq and 13 ft high. Air under 10-lb pressure is introduced into the bottom of each tank through 16 equally spaced ¼-in. diam orifices. Air is supplied with a Fuller rotary air compressor. The charge is heated with live-steam jets. After leaching is completed, the leached slimes again are thickened and then washed free of electrolyte by settling and decantation in five tanks located on the 3rd floor and 2nd floor mezzanine. These slimes then are filtered on a 3x4-ft Oliver drum filter that discharges directly upon a gas-fired Lowden drier, with a 4x27-ft hearth, located on the 2nd floor. The leached slimes are dried to about 10 pct moisture before being discharged into a tilting double-cone mixer, on the 1st floor, from which they are dumped, sampled, and then packaged in iron drums.

All of the liquor from the leaching operations is returned to the tank house after it has been processed to remove small amounts of selenium and tellurium which go into solution. This is a cementation process using tank house stripper scrap.

The packaged slimes are shipped to the United States Metals Refining Co., Carteret, N. J., for further treatment.

### Blue Vitriol Plant

This plant not only provides a means for purifying the tank house electrolyte, but also is capable of producing more than 1100 tons per month of copper sulphate that will assay not less than 99.0 pct  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

The building is north of and adjacent to the slimes treating plant. It consists of a 54x115-ft main building with three floors and a basement, a main floor 47x134-ft west extension, a main floor 16x77-ft east extension, and a 40x100-ft quonset storage building. On the north side of the plant is a 15x149-ft shipping platform serviced by a standard gage railroad siding. The walls of the main building are made of

red hollow tile, and the two extensions have R.P.M. siding. All floors are reinforced concrete.

The electrolyte withdrawn from the tank house is stored in two storage tanks in the basement. This electrolyte is pumped to two oxidizing units on the 3rd floor. Each unit consists of two lead-lined steel towers for shot copper elevated so they will drain into a single charge tank. A charge to each unit amounts to about 52,000 lb of electrolyte. The solution is withdrawn intermittently from the charge tank and sprayed into the top of the shot towers, that are filled with shot copper, by means of an air lift operating under a maximum pressure of about 65 lb. Air is blown up through the shot copper under a pressure of about 4 lb. The solution drains down through the shot copper and back into the charge tank. The solution is heated in the charge tank with live-steam jets and circulated in the above manner until the free acid has been neutralized by converting it to copper sulphate, this usually requires about 12 hr per charge. This charge is pumped to a holding tank on the 3rd floor from which it flows by gravity to a filter press on the 2nd floor where the float slimes are removed. The filtered liquor is pumped to one of five atmospheric evaporators on the 3rd floor where it is evaporated to about 49 Bé. Each evaporator is equipped with eight double 100-ft steam coils made of 1-in. diam lead pipe which are operated under 30 lb pressure. Then this liquor is put into atmospheric coolers, one charge from an oxidizer unit ultimately filling a cooler.

The coolers are lead-lined steel tanks. The inside dimensions are about 7½x16½x4½ ft with ends curved on a radius of 3¾ ft and they have a working capacity of about 500 cu ft. There are 16 coolers on the 2nd floor and 15 coolers on the main floor west extension. A total of 180, ¾x48-in. round copper rods are spaced equally and suspended vertically in each cooler on 2x4-in. boards supported by iron tee bars. A drain in the form of a plug seat is provided in the center of each cooler bottom.

The coolers are operated normally on either a six or seven day cycle depending upon production demands, and each cooler will produce an average of about 8 tons of copper sulphate per cycle. About one day of each cycle is required for draining the cooler, cleaning out the copper sulphate crystals that form on the rods, sides, and bottom, and refilling it. When the crystals are removed from the coolers, they are placed in 30-in. gage side-dump cars of about 3000-lb capacity, trammed by hand to a 6000-lb capacity elevator, and taken to the 3rd floor where they are dumped through grizzlies into storage bins, the bottom crystals being kept separate from the rods and sides crystals. The sides and rods crystals are crushed with a finger crusher, screened through a 3x8-ft vibrating triple-deck Niagara screen located on the 2nd floor, in order to separate or grade the crystals according to size, and stored in bins on the main floor from which they are bagged. The bottom crystals are crushed with a saw-tooth crusher, washed and centrifuged dry, and blended with the other crystals on the screens. The bagged crystals are handled and stored on wooden pallets by using a Clark fork-lift truck.

First mother liquors are evaporated to make second crystals, which are also of commercial grade. Second mother liquors are evaporated to make third crystals, which are dissolved with distilled water in an agitator and the solution returned to the oxidizing units. Third mother liquors are sent to cementa-



tion tanks where the copper that remains in solution is removed with iron. The waste liquor is discarded and the cement copper sent to the Phelps Dodge smelter at Douglas, Ariz.

The east main floor extension houses a Raymond No. 32 impact pulverizer equipped with a drier fired with natural gas, cyclone collector, mechanical separator, and Dracco collector. This equipment will convert about 600 lb of blue vitriol per hour into —300-mesh Instant or Monohydrate copper sulphate.

Shot copper for the process is produced at the Douglas smelter from converter copper. It is received in railroad box cars and unloaded through hatches on the shipping platform into storage bins, located in the blue vitriol plant basement. It is trammed to the top of the shot towers by means of bottom-dump 30-in. gage cars and a 5000-lb capacity elevator.

### Casting and Inspection

The building, which houses the casting, inspection and shipping departments, and also the cathode shears and wire-bar scalping machine, is 479 ft long and 207 ft wide and is directly south of the tank house, the charging floor being on the same level as the tank house basement. The intervening yard space, which is 220 ft wide, provides ample room for the two yard scales and setting-up furnace charges. The building has two levels: Namely, the charging and furnace level, and a casting, inspection, shipping, shearing, and scalping level, the difference in elevation is 7 ft. The sides of the building are covered with Tennessee galvanized copper-steel sheathing and the roof is cast gypsum except for the metal roofing directly over the furnaces.

The charging bay is 40 ft wide and is equipped with two 3½-ton Morgan overhead charging cranes and one 5-ton Milwaukee overhead service crane. The pole storage area is outside of the building at the east end of the charging bay. The furnace bay is 24 ft wide. The reverberatory anode furnace has a capacity of 225 tons and is equipped with a 600-hp waste-heat boiler. Two wire-bar furnaces have a capacity of 385 tons each and are equipped with 600-hp waste-heat boilers. A third wire-bar furnace has a capacity of 400 tons and is equipped with a 1200-hp waste-heat boiler.

Anode and wire-bar furnaces have inverted-arch, silica brick bottoms; hard-burned magnesite brick below the metal line; chemically bonded brick in back wall, throat, and uptake; and 15-in. silica brick in the hood and main roof. The verb arch and the supporting arch for the uptake are of magnesite-chrome mixture brick. The buckstays at the charging side are protected by steel water-cooled pads. At the charging doors, two on the anode and three on the wire-bar furnaces, the buckstays are protected from the furnace heat, when the doors are open, by heavy castings bolted to the buckstays. The charging doors, which are water-cooled on the sides and bottom, are lined with fire brick and operated by air hoists. Water-cooled flange steel skewbacks are used on the charging side of the furnaces and cast iron skewbacks on the back wall side. All water used for skewbacks is treated with Calgon and this has minimized scale and skewback failures.

Natural gas, which is used for fuel, is delivered to the plant at 350-lb pressure, is reduced to 35 lb in the meter house and is at about 30 lb when it reaches the furnaces. The anode furnace and two of

the wire-bar furnaces are equipped with Coppus-Dennis burners, two on the anode and three on the wire-bar furnaces. The third wire-bar furnace is equipped with three Tate-Jones, cement-kiln type, low-pressure burners. Two wire-bar furnaces have pre-heaters for raising the temperature of the air for combustion. The combustion air from two 10,000 cu ft forced-draft fans passes through carborundum tubes which are heated by the combustion gases passing around these tubes on their way to the main balloon flue and 410-ft stack. The anode and one wire-bar furnace have bypass or auxiliary stacks that have a height of 78 and 91 ft, respectively, above the charging floor.

The casting and inspection bay, 67½ ft wide, is serviced with two 15-ton overhead Milwaukee cranes and one 15-ton overhead Shaw-Box crane.

Anodes are cast in 20 copper moulds on a 31-ft diam Clark wheel with a single ladle that is controlled electrically. Pulverized silica, 200 mesh, is used to paint the moulds. The copper insert blocks for the Baltimore groove are cast by the furnace crew. Two push pins activated by a toggle arrangement raise the anodes from the moulds. A ½-ton Shaw bosh crane removes the anodes from the moulds and places them on spaced racks in the bosh. An overhead crane removes the anodes from the bosh with a rack similar to the rack used in the tank house. After inspection, the anodes are placed in an anode rack car and transported to the receiving department for weighing and sampling before they are stocked or delivered to the tank house.

Wire bars, ingot bars, and ingots are cast on three 40-ft diam Clark wheels, each having 30 copper moulds and using two ladles, all of which are controlled electrically. The moulds are painted by spraying a water and bone ash emulsion with high-pressure air. The moulds are turned over by means of a dumping-tee mechanism and the cast shapes fall into a bosh pit where they are quenched. An incline conveyor brings the cast shapes up out of the bosh pit to an inspection conveyor where the copper inspectors gage each piece for size and make a rigid inspection for defects. The wire bars are removed from the inspection conveyor with air hoists and loaded on cars which are delivered to the shipping department. Ingot bars and ingots are removed from the inspection conveyor by hand and placed on wooden pallets which are delivered by powered fork-lift trucks to the shipping department. Rejected pieces are placed to one side for remelting.

A mould press on each wire-bar furnace having water-cooled copper wire-bar dies is used to make the copper moulds required for the various sizes of wire bars. A portable tilting ladle is used to cast anode moulds.

A charge for the anode furnace consists of anode scrap from the tank house, blister, ladle scrap, and No. 2 and Light custom scrap. A wire-bar furnace charge consists of cathodes, No. 1 custom scrap, ladle scrap, moulds, warmers, and rejects. The furnaces are operated on a 24-hr cycle. This cycle, which begins early in the afternoon, consists of charging, melting, skimming slag, flapping, covering charge with coke, poling until the copper has reached the required set, and casting the copper into shapes. Flapping is done with iron pipes using air under 20-lb pressure. Poling is with green, hardwood poles.

Fire-refined copper cast into ingots and ingot bars is produced from the wire-bar furnaces by charging



them with carefully selected high-purity copper.

Samples are taken of the castings from all furnace charges and analyses made for Cu, Ag, Au, and impurities. The conductivity of the copper is also determined.

Slags are broken up and stored in an outdoor area at the east end of the shipping bay. They are shipped in gondola cars to the Douglas smelter. Moulds are stored in an outdoor area 82 ft long at the west end of the casting and inspection bay which is serviced by the overhead crane in the west end of this bay.

A building at the eastern end of the yard area between the tank house basement and the charging floor provides storage facilities for stocks of brick, fire clay, silica, bone ash, charcoal, and other supplies for the anode and wire-bar furnaces. This building is of hollow tile construction and is 39x260 ft. A standard gage railroad siding parallels the south side of the building. Coke is stored in an open area east of this building.

A brick-grinding plant, just east of the furnace bay, is equipped with a jaw crusher, Gruendler grinder, Raymond impact pulverizer, and a bag-type dust collector. This equipment is used to grind silica, magnesite, and chrome brick cobbings for furnace repairs.

### Shipping

The shipping bay, south of and adjacent to the casting and inspection bay, extends the full length of the building and is 60 ft wide. This, together with an outside storage area of the same width and 165 ft long, at the west end of the bay, provides ample storage for refined shapes. This bay and storage area is serviced with one Euclid, one P & H, and one Milwaukee overhead crane, each having a capacity of 10 tons. Three track scales of 20-ton capacity each are provided for weighing copper. Two "Ready Power" motor-powered trucks and three Baker trucks powered with Edison batteries, all of which are the fork-lift type, are used for handling palletized ingots and ingot bars and for loading all kinds of refined shapes into railroad cars. A shipping platform 15½ ft wide and 594 ft long is parallel with and adjacent to the south side of the shipping bay and outside storage area.

### Cathode Shears and Scalping Machine

Two Hilles-Jones shears for shearing cathodes are at the east end of the shipping bay. Each shear consists of a large shear for cutting off loops and making the first cut and a small cut-off shear which makes the final cuts. When producing 12½x17½-in. cathodes, each shear will cut 220,000 lb of cathodes per 8-hr shift.

An Ingersoll single head, custom built, scalping machine is also in the shipping bay. This machine will scalp 275—54-in.—wire bars per 8-hr shift. Just enough copper is cut from the set side of the wire bars to remove the roughness which is characteristic and appears at this surface.

### Warehouse and Shops

The warehouse is 69 ft south of the eastern portion of the shipping platform and is of hollow-tile construction. It consists of a building 39x240 ft with an unloading platform 15x220 ft serviced by a standard gage railroad siding.

The shops are 31 ft south of the western portion of the shipping platform and 80 ft west of the warehouse. The building is of hollow-tile construction, is 57x280 ft, and houses the machine, blacksmith,

electrical, and carpenter shops equipped with the machines and tools necessary for the maintenance of a plant of this type.

### Power

All of the electric power for the plant is purchased from the El Paso Electric Co. Alternating current is delivered at 13,200 v and stepped down to 2300 v at the plant substation.

A brick building, 51x144 ft, with the main floor 15 ft above the ground floor, houses the direct-current power generating equipment for electrolysis. The air-conditioning and armature-cooling equipment, bus bars, and switchgear are on the ground floor. The motor-generator sets, control equipment, and four air compressors are on the elevated main floor. This floor is serviced with a 15-ton Bedford overhead crane, and an open bay at the east end of the building facilitates the removal and installation of heavy equipment. The building is located centrally 73 ft south of the tank house.

Direct current is produced with three double unit and two triple unit General Electric motor-generator sets, each dc generator unit having a capacity of 750 kw and an output of 5000 amp at 150 v. A full tank house requires the operation of two double and two triple sets, as each of the three electrical circuits in the tank house require nearly 15,000 amp. The other double set is held as a standby. Except for the motor-generator sets, which operate on 2300 v, practically all of the electric motors in the plant are operated on 440 v. A standard 220-110 v, three wire, single-phase lighting system is used.

The four Ingersoll-Rand air compressors supply compressed air for general plant requirements. Two of these are low-pressure compressors, each having a capacity of 1080 cfm at 40 psi. The other two are high-pressure compressors, each having a capacity of 1210 cfm at 100 psi.

### Water Supply and Treatment

All of the water required for plant operations is obtained from three 700-ft water wells equipped with Layne-Texas turbine-type pumps. These pumps deliver water to three tanks having a total capacity of one million gallons. Two of these tanks are elevated in order to maintain about 30-lb pressure in all of the fresh water lines. An electrically driven pump and one driven with an internal-combustion engine, which is used in case of a power failure, boost the pressure in the water lines to as much as 125 lb for fire-fighting purposes.

All of the water pumped from the three wells is given the Hall Threshold treatment. The boiler feed-water is treated by the Infilco hot lime-soda ash and the Hall system.

### General

The general office building, west of the shops near the main plant entrance, houses the administrative, accounting, and engineering offices, and a well-equipped laboratory.

Another building, at the main plant entrance, houses the time-clock alley, personnel and safety engineering offices, and clinic for first-aid treatment.

### References

<sup>1</sup> Frank R. Corwin and C. S. Harloff: El Paso Refinery of the Nichols Copper Company. *Mining and Metallurgy* (1930) **11**, pp. 459-465.

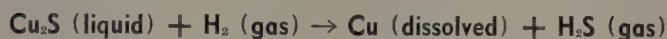
<sup>2</sup> Expanded Copper Refinery. *Mining World* (Sept. 1945) **7**, No. 10, pp. 15-20.



# Sulphur Activities in Liquid Copper Sulphides

by R. Schuhmann, Jr. and O. W. Moles

An equilibrium study was made of the reaction:



at temperatures of 1150°, 1250°, and 1350°C for liquid copper sulphides ranging in composition from saturation with Cu to about 21.5 pct S. From the experimental data, activities of Cu, S, and  $\text{Cu}_2\text{S}$  in the melts were calculated. Also, the results furnish a new determination of the location of the curve showing the compositions of Cu-saturated sulphide melts in the Cu-S constitution diagram.

THE "white metal" made as an intermediate product in converting copper matte to blister copper is a matte approximating  $\text{Cu}_2\text{S}$  in composition. It has long been known that liquid Cu-S mattes can exist at a given temperature over an appreciable composition range, with S:Cu ratios ranging up from a lower limit corresponding to equilibrium of the matte with a liquid Cu phase. The Cu-saturated matte has somewhat less S than  $\text{Cu}_2\text{S}$ , although previous measurements of the compositions of Cu-saturated mattes are not in good agreement.<sup>1-4</sup> As the S:Cu ratio approaches and slightly exceeds that for  $\text{Cu}_2\text{S}$ , the partial pressure of sulphur gas over the liquid matte rapidly approaches atmospheric pressure,<sup>5</sup> so that Cu-S melts with much more S than  $\text{Cu}_2\text{S}$  can be made and handled only in pressure apparatus. Accordingly, the liquid copper sulphides of interest in copper smelting and readily studied experimentally fall in a relatively narrow composi-

tion range about  $\text{Cu}_2\text{S}$ . The freezing points of Cu-S mattes show a maximum of 1129°C near the composition  $\text{Cu}_2\text{S}$ , dropping to 1105°C for Cu-saturated mattes having less S and dropping under 1100°C for higher S mattes.<sup>4</sup>

Estimates of the sulphur pressure and other thermodynamic properties of liquid  $\text{Cu}_2\text{S}$  were made by Kelley,<sup>6</sup> based on extrapolations from equilibrium measurements on solid  $\text{Cu}_2\text{S}$ . More recently, Cox and coworkers<sup>7</sup> studied equilibria in the reaction:



over the temperature range 700° to 1250°C. They measured equilibrium  $\text{H}_2\text{S}:\text{H}_2$  ratios presumably with both the sulphide and the metal phase present, so that their data above the melting point of  $\text{Cu}_2\text{S}$  should measure the S pressure of Cu-saturated sulphide melts. The sulphur pressures of liquid copper sulphides of several S:Cu ratios at their freezing points can be estimated from data given by Posnjak, Allen, and Merwin.<sup>8</sup> However, beyond these few data, no systematic study seems to have been made of the relations of sulphur pressure and other chemical properties of liquid copper sulphides to composition and temperature.

The measurements of the sulphur pressures of liquid copper sulphides reported in this paper represent a first step in the quantitative study of the chemistry of mattes. Similar work is planned on

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This paper represents part of a thesis by O. W. Moles submitted in partial fulfillment of requirements for the degree of Doctor of Science to the Faculty, Massachusetts Institute of Technology.

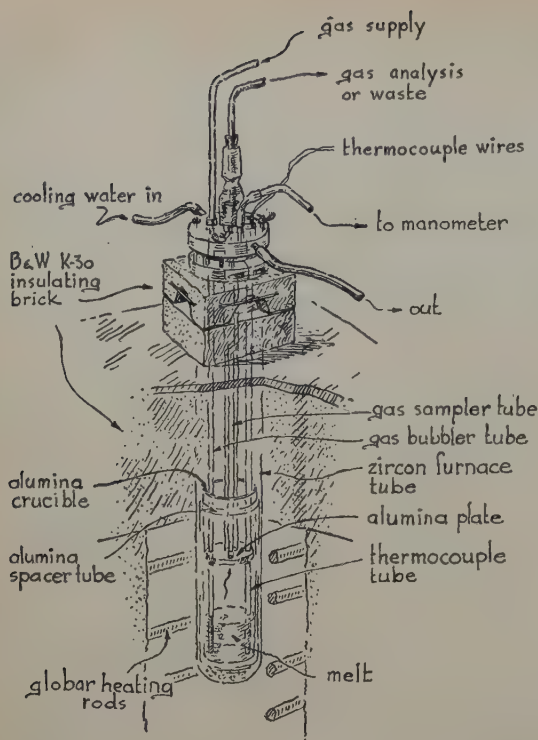


Fig. 1—Furnace tube assembly.

Cu-Fe-S mattes and on mattes containing oxygen. The relationship of these studies to other aspects of copper-smelting chemistry was discussed in an earlier paper by one of the authors.<sup>8</sup>

The experimental work of the present investigation consisted of measurements of  $H_2S:H_2$  ratios for gas mixtures in equilibrium with liquid copper sulphides. These measurements were made for melts of varying S content, from Cu-saturation to compositions having the highest S activities conveniently determinable with  $H_2S/H_2$  mixtures. The actual composition range covered was about from 19.5 to 21.5 pct S (balance Cu) and the temperature range was from 1150° to 1350°C. In addition, equilibrium  $H_2S:H_2$  ratios were determined for systems containing the two mutually saturated phases, liquid Cu and liquid  $Cu_2S$ . From the experimental data, calculations were made of the  $S_2$  pressures and of the activities of Cu and  $Cu_2S$ . Also the data furnished a new determination of the curve showing the compositions of Cu-saturated copper sulphides in the Cu-S equilibrium diagram.

### Experimental Methods

The general procedure of equilibrium measurement was as follows: A controlled mixture of  $H_2S$  and  $H_2$  was bubbled through the Cu-S melt in a

Table I. Reproducibility of Gas Analyses

| H <sub>2</sub> S, Pct |       |      |      |      |      |       |       |       |       |
|-----------------------|-------|------|------|------|------|-------|-------|-------|-------|
| A                     | B     | C    | D    | E    | F    | G     | H     | I     | J     |
| 1.010                 | 0.453 | 1.59 | 1.02 | 2.51 | 5.01 | 0.501 | 0.364 | 0.424 | 1.531 |
| 1.024                 | 0.448 | 1.62 | 1.04 | 2.51 | 5.03 | 0.510 | 0.361 | 0.416 | 1.545 |
| 1.002                 | 0.441 | 1.60 | 1.04 | 2.51 | 5.00 | 0.500 | 0.362 | 0.419 | 1.539 |
|                       |       |      |      |      | 5.03 | 0.498 | 0.355 |       |       |
|                       |       |      |      |      |      | 0.498 | 0.363 |       |       |
|                       |       |      |      |      |      | 0.496 |       |       |       |

closed furnace system. Analyses were made of the entrant and exit gases. The composition of the entrant gas mixture was adjusted until the  $H_2S:H_2$  ratios in entrant and exit gases were equal and remained equal for several hours. The final  $H_2S:H_2$  ratio thus found was considered to be the equilibrium ratio. After equilibrium was established in this way, samples of the melt were taken and analyzed chemically for S and Cu.

**Furnace Arrangement:** Fig. 1 shows the principal features of the furnace arrangement. The furnace tube was a zircon tube, 20 in. long x 3 in. in diam outside, with one end closed (test tube shape). This tube was suspended vertically in a Global furnace, with the bottom of the tube just below the thermal center of the furnace and the top projecting through the top of the furnace. The mouth of the furnace tube was closed with a brass, water-cooled head provided with openings for sealing in the various gas inlet and exit tubes and the thermocouple protection tube. This assembly was substantially gas tight at operating temperature.

The principal parts inside the furnace tube were all of high quality alumina, and the crucible, protection tubes, and gas tubes were made of pure dense alumina (Norton Co.). The space above the crucible was filled with hollow alumina pellets as insulating material. The crucible was 2x8 in. and normally contained a melt of about 250 g which filled it to a depth of about 1 in. No chemical attack or penetration of the crucible or other parts by the melt was found, and in six weeks' continuous operation at 1150° to 1350°C the only deterioration in the system was erosion of the lower end of the bubbling tube. Referring to Fig. 1, the normal path of gas flow was into the crucible through the bubbler tube and then out through the gas sampler tube. For initial flushing of the furnace tube as a whole, however, the gas was taken out through a connection in the brass head, labeled "to manometer" in Fig. 1. The normal gas flow rate into the system was 120 ml per min.

The furnace was constructed of K-30 insulating bricks in a sheet steel shell, and measured 8 in. sq x 13½ in. high inside. Eight ½-in. Globar elements furnished the heat. A Rayotube sighted through a peephole onto the zircon furnace tube was connected to a Micromax recorder-controller panel with a Leeds and Northrup position-adjusting control unit. The control unit in turn was connected to a Leeds and Northrup valve-operating mechanism mounted on a General Electric induction regulator to control automatically the power input to the furnace. With this arrangement, furnace temperatures readily were maintained constant for long periods to within about 2°C.

Melt temperatures were measured with Pt—Pt-Rh thermocouples calibrated at the gold point by the wire-bridge method. Final equilibrium temperatures were checked with two couples, each inserted in turn into the bottom of the protection tube in the melt, as shown in Fig. 1. The maximum difference between the two couples was 2°C, and most of the duplicate readings checked within 1°C.

**$H_2S/H_2$  Mixtures:** The gas mixtures fed to the furnace ranged from 0.3 to 100 pct  $H_2S$ , the balance  $H_2$ . The  $H_2S$  and  $H_2$  passed from their supply tanks through separate purification trains and flowmeters before mixing. The  $H_2$  (electrolytic) was passed over a palladium catalyst and then through calcium sul-



phate and phosphorus pentoxide drying tubes. The  $\text{H}_2\text{S}$  (Matheson, 99.9 pct) was simply dried over phosphorus pentoxide. Constant composition of the gas mixture was obtained by automatically maintaining constant pressure drops across the flowmeters, using three bubbler-type pressure regulators, one upstream of each flowmeter and one on the mixed gas downstream from both flowmeters. Sized glass powders, compacted and sintered in glass tubes, were used for flow resistances in the flowmeters. Dow-Corning 550 silicone oil was used in the manometers and pressure regulators so that the system could be dried thoroughly. The gas trains were of all glass construction, except for short connections at the supply tanks and furnace.

**Gas Analyses:** The  $\text{H}_2\text{S}/\text{H}_2$  gas mixture entering and leaving the furnace was analyzed by a method based on the fractional distillation of  $\text{H}_2$  from  $\text{H}_2\text{S}$  in vacuum at liquid nitrogen temperatures. The analytical apparatus is shown in Fig. 2. The procedure was as follows: Evacuate the bulb; collect a sample in the bulb, preferably flushing with at least 10 volumes of gas, about 1 liter, to bring the glass and stopcock grease to equilibrium with the sample; measure the pressure and temperature of the  $\text{H}_2\text{S}/\text{H}_2$  mixture; freeze the  $\text{H}_2\text{S}$  by immersing the bulb in liquid nitrogen and pump off the hydrogen, to less than 10 microns pressure; close the bulb, evaporate the  $\text{H}_2\text{S}$ , and return it to the original temperature of the gas mixture; measure the pressure of the  $\text{H}_2\text{S}$ , which is the partial pressure of the  $\text{H}_2\text{S}$  in the original gas mixture. For low percentages of  $\text{H}_2\text{S}$ , the  $\text{H}_2\text{S}$  was compressed into the smaller bulb before measuring its pressure. The ratio of the volume of the small bulb to the total volume of the two bulbs was determined by a calibration using  $\text{H}_2\text{S}$ . Corrections were made for the nonideality of the gases.

In developing this analytical method, a variety of tests were carried out. One check of the accuracy of the procedure consisted in analyzing known mixtures prepared in the bulb by admitting pure  $\text{H}_2$  and  $\text{H}_2\text{S}$  successively, measuring the pressure after each addition. Another series of tests showed that no  $\text{H}_2\text{S}$  was lost after repeated freezing with liquid nitrogen and evacuation. Table I gives the results of repeated check analysis for ten different gas compositions ranging from 0.36 to 5 pct  $\text{H}_2\text{S}$  and shows the good reproducibility obtained.

**Sampling and Analyses of Melts:** Melts were sampled using 7 mm vycor tubing with the sampling end closed to the size of a pinhole. The sampling tube was lowered into the furnace after removing the gas sampling tube. Gas was slowly drawn up through the tube to flush out air. The end was then lowered into the melt and a sample sucked into the tube. Each time 10 to 25 g were secured. For two-phase melts, the gas bubbler tube was raised and the melt allowed to settle an hour before sampling.

All samples were chemically analyzed for both copper and sulphur. The electrolytic method was used for copper. Allen and Bishop's<sup>9</sup> method, involving weighing the sulphur as barium sulphate, was used for sulphur. Difficulties were encountered in obtaining the precision desired in the sulphur determinations, so that on some samples several repeats were necessary to obtain checks. In the end, the sulphur figures obtained by duplicate chemical analyses were checked against the copper analyses (by difference) and, for sulphur contents below

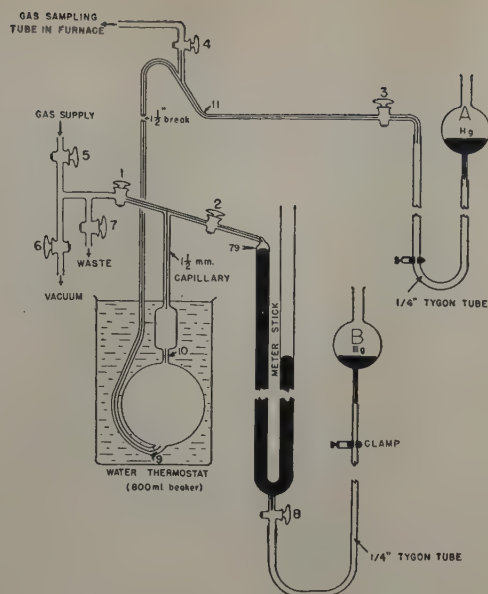


Fig. 2—Gas analysis apparatus.

20.14 pct (pure  $\text{Cu}_2\text{S}$ ), were checked against analyses made by a pycnometer method.

$\text{R}_2\text{O}_3$  analyses on eight melts varied from 0.026 to 0.077 pct, averaging 0.048 pct. Iron analyses of six melts varied from 0.008 to 0.029 pct ( $\text{R}_2\text{O}_3$  includes  $\text{Fe}_2\text{O}_3$ ). These data showed the absence of melt contamination by the refractories.

**Materials:** A supply of high-purity copper was furnished by the Central Research Laboratory of the American Smelting and Refining Co. and analyzed as follows: 0.0015 pct Fe, 0.001 pct Sb, 0.0009 pct Pb, 0.0003 pct Sn, 0.0015 pct Ni, 0.00009 pct Bi, 0.001 pct As, and 0.0002 pct Te. A stock of copper sulphide was prepared by treating pieces of this copper with precipitated sulphur (U.S.P., Mallinckrodt) in a casserole heated over a laboratory burner. No precautions were taken to exclude oxygen, since any oxygen was removed as  $\text{H}_2\text{O}$  during the early stages of treatment with  $\text{H}_2\text{S}/\text{H}_2$  mixtures in the furnace. The stock copper sulphide analyzed 78.5 pct Cu.

### Experimental Results and Calculations

**Blank Runs:** Since comparison of entrant and exit gas compositions was used as the criterion of gas-melt equilibrium, it was necessary to establish the absence of side reactions in the furnace system. Accordingly, a number of runs were made passing various  $\text{H}_2\text{S}/\text{H}_2$  mixtures through the complete furnace system at temperature, but without copper sulphide in the crucible. Results of these preliminary runs may be summarized as follows:

1—A newly assembled furnace system required a break-in period of several days passing  $\text{H}_2\text{S}/\text{H}_2$  mixtures at temperature. During this period some  $\text{H}_2\text{O}$  was present in the exit gas. Also the  $\text{H}_2\text{S}:\text{H}_2$  ratio was lower in the exit gas, indicating some accumulation of sulphur in the furnace parts.

2—After the break-in period, from 8 to 24 hr operation was required to bring the furnace to equilibrium with the gas after a major change in entrant gas composition.

3—To obtain equality of entrant and exit gas compositions, all the exit gas had to be removed

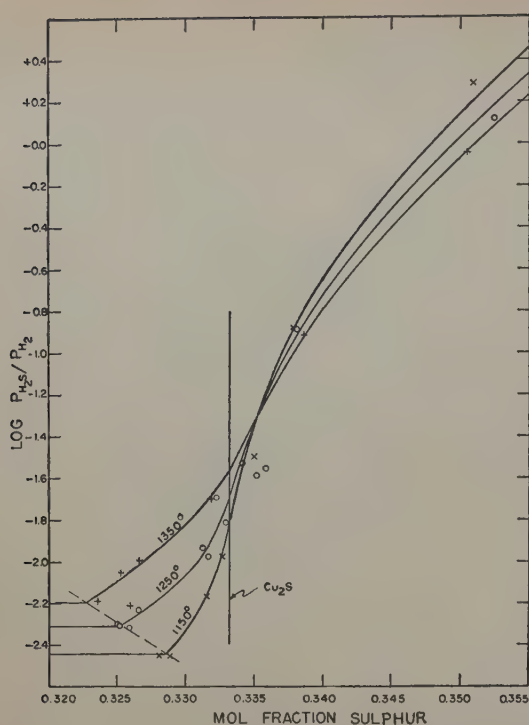


Fig. 3—Log  $p_{H_2S}/p_{H_2}$  vs. mol fraction sulphur at 1150°, 1250°, and 1350°C.

from the hot zone in the crucible through the gas sampling tube, shown in Fig. 1. When part was removed this way and part through the tube in the top of the furnace, to obtain quicker flushing, thermal separation took place so that the gas removed from the hotter zone was lower in  $H_2S$  than the ingoing gas.

The preliminary runs also indirectly shed some light on the effects of the dissociation of  $H_2S$  in the furnace. Within the crucible it is to be expected that equilibrium will be established in the dissociation reaction,  $H_2S \rightleftharpoons \frac{1}{2}S_2 + H_2$ . The entering gas mixture contained only  $H_2S$  and  $H_2$ , so that the  $S_2$  must be furnished by dissociation of  $H_2S$  with a resultant change in the  $H_2S:H_2$  ratio. For this reason, the  $H_2S:H_2$  ratios measured by analysis at room temperature had to be corrected for dissociation to obtain the equilibrium values of the  $H_2S:H_2$  ratios for the furnace conditions. However, the question arises as to what happened to the gas flowing out the exit tube. The hot gas entering this tube presumably was an equilibrium mixture of  $H_2$ ,  $H_2S$ , and  $S_2$ . The absence of appreciable sulphur deposition in the colder parts of the gas exit, together with the fact that in the preliminary runs equality of  $H_2S:H_2$  ratios was obtained between entrant and exit gases, indicated that very high reaction rates were obtained so that the  $S_2$  recombined with  $H_2$  in the short time of passage of the gas through the exit tube. This behavior was essential if a comparison of entrant and exit gas analyses was to serve as the criterion of equilibrium. When the  $H_2S$  content of the entrant gas was increased to 100 pct for the final equilibrium runs on high sulphur melts, however, appreciable sulphur deposition occurred and the exit gas never reached 100 pct  $H_2S$ , although it appeared from other grounds that gas-melt equilibrium had been established in the crucible.

**Equilibrium Measurements:** In all, 32 equilibrium determinations were made, the first four in one continuous run lasting ten days and the remaining 28 in a second run lasting six weeks. Each determination involved many gas analyses and adjustments of ingoing gas composition to find the equilibrium condition. After adjustments appeared to be completed in each determination, bubbling was continued for several hours with additional gas analyses to check the existence of equilibrium before taking final samples of the melt. A number of the equilibrium gas analyses were approached from both sides. From the general behavior of the system, it appeared that gas-melt reaction was very rapid so that the rather long time spent in reaching equilibrium after a change was needed mainly to bring the furnace

Table II. Experimental Data

| Point No.                                                            | Time of Sampling, Hr* | Temperature, °C | Final Gas Analyses, Pct H <sub>2</sub> S |       | Melt Analyses, Wt Pct |        |
|----------------------------------------------------------------------|-----------------------|-----------------|------------------------------------------|-------|-----------------------|--------|
|                                                                      |                       |                 | In                                       | Out   | Cu                    | S      |
| Run I                                                                |                       |                 |                                          |       |                       |        |
| 200 g Cu <sub>2</sub> S stock charged at the start                   |                       |                 |                                          |       |                       |        |
| 1                                                                    | 28                    | 1296            | 2.05                                     | 2.04  | 79.74                 | 20.06  |
| 2                                                                    | 58                    | 1236            | 1.63                                     | 1.63  | 79.76                 | 20.09  |
| 50 g Cu <sub>2</sub> S added                                         |                       |                 |                                          |       |                       |        |
| 3                                                                    | 198                   | 1154            | 1.049                                    | 1.061 | 79.77                 | 20.06  |
| 5 g Cu added                                                         |                       |                 |                                          |       |                       |        |
| 4                                                                    | 246                   | 1155            | 0.704                                    | 0.691 | 79.73                 | 19.95  |
| Access tube broken. Furnace shut down.                               |                       |                 |                                          |       |                       |        |
| Run II                                                               |                       |                 |                                          |       |                       |        |
| 250 g Cu <sub>2</sub> S charged                                      |                       |                 |                                          |       |                       |        |
| 5                                                                    | 27                    | 1243            | 2.94                                     | 2.92  | 79.73                 | 20.18  |
| 6                                                                    | 92                    | 1243            | 2.78                                     | 2.77  | 79.62                 | 20.30  |
| 7                                                                    | 136                   | 1243            | 2.56                                     | 2.54  | 79.67                 | 20.25  |
| 5.7 g Cu added                                                       |                       |                 |                                          |       |                       |        |
| 8                                                                    | 265                   | 1249            | 1.018                                    | 1.041 | 79.98                 | 20.02  |
| 4.8 g Cu added                                                       |                       |                 |                                          |       |                       |        |
| 9                                                                    | 289                   | 1251            | 0.587                                    | 0.587 | 80.33                 | 19.64  |
| 5.5 g Cu added                                                       |                       |                 |                                          |       |                       |        |
| 10                                                                   | 377                   | 1253            | 0.527                                    | 0.506 |                       |        |
| 5.2 g Cu added                                                       |                       |                 |                                          |       |                       |        |
| 11                                                                   | 427                   | 1253            | 0.522                                    | 0.509 | 80.28                 | 19.49  |
| 100 g Cu added                                                       |                       |                 |                                          |       |                       |        |
| 12                                                                   | 449                   | 1254            | 0.491                                    | 0.508 | 80.43                 | 19.54  |
| 13                                                                   | 525                   | 1356            | 0.668                                    | 0.657 | 80.41                 | 19.40  |
| 14                                                                   | 556                   | 1156            | 0.457                                    | 0.366 | 80.15                 | 19.74  |
| Removed melt, 145 g<br>New charge: 325 g Cu, 275 g Cu <sub>2</sub> S |                       |                 |                                          |       |                       |        |
| 15                                                                   | 579                   | 1156            | 0.360                                    | 0.365 | 80.15                 | 19.81  |
| 16                                                                   | 603                   | 1205            | 0.437                                    | 0.426 | 80.27                 | 19.63  |
| 17                                                                   | 629                   | 1253            | 0.512                                    | 0.492 | 80.50                 | 19.63  |
| 18                                                                   | 672                   | 1306            | 0.593                                    | 0.563 | 80.17                 | 19.75  |
| 19                                                                   | 693                   | 1359            | 0.646                                    | 0.649 | 80.35                 | 19.60  |
| 356 g melt removed                                                   |                       |                 |                                          |       |                       |        |
| 200 g Cu <sub>2</sub> S added                                        |                       |                 |                                          |       |                       |        |
| 20                                                                   | 747                   | 1361            | 0.921                                    | 0.932 | 80.51                 | 19.58  |
| 20 g Cu <sub>2</sub> S added                                         |                       |                 |                                          |       |                       |        |
| 21                                                                   | 770                   | 1360            | 1.098                                    | 1.091 | 80.29                 | 19.65  |
| 30 g Cu <sub>2</sub> S added                                         |                       |                 |                                          |       |                       |        |
| 22                                                                   | 793                   | 1359            | 2.06                                     | 2.07  | 79.88                 | 20.03  |
| 23                                                                   | 818                   | 1256            | 2.06                                     | 2.07  | 79.92                 | 20.06  |
| 1.5 g Cu added                                                       |                       |                 |                                          |       |                       |        |
| 24                                                                   | 858                   | 1257            | 1.17                                     | 1.199 | 79.99                 | 19.98  |
| 100 g Cu <sub>2</sub> S added                                        |                       |                 |                                          |       |                       |        |
| 25                                                                   | 889                   | 1157            | 1.541                                    | 1.566 | 79.89                 | 20.11  |
| 26                                                                   | 912                   | 1159            | 3.08                                     | 3.08  | 79.70                 | 20.25† |
| 100 g Cu <sub>2</sub> S added                                        |                       |                 |                                          |       |                       |        |
| 27                                                                   | 932                   | 1159            | 11.75                                    | 11.76 | 79.50                 | 20.45† |
| 28                                                                   | 939                   | 1263            | 11.71                                    | 11.71 | 79.48                 | 20.47† |
| 100 g Cu <sub>2</sub> S added                                        |                       |                 |                                          |       |                       |        |
| 29                                                                   | 952                   | 1362            | 11.57                                    | 11.65 | 79.44                 | 20.51† |
| 30                                                                   | 960                   | 1360            | 100.0                                    | 89.0  | 78.57                 | 21.38† |
| 31                                                                   | 977                   | 1165            | 100.0                                    | 87.0  | 78.53                 | 21.42† |
| 32                                                                   | 985                   | 1258            | 100.0                                    |       | 78.42                 | 21.53† |

\* For each run, zero time was at the end of several days' operation of the furnace at temperature with an  $H_2S/H_2$  atmosphere.

† By difference from Cu analysis, allowing 0.05 pct for impurities.



system itself, apart from the melt, to equilibrium under the new conditions.

Table II summarizes the log of the experimental work. Points 1 to 9 and 20 to 32, inclusive, represent equilibria of the gas mixtures with liquid copper sulphides of varying S content up to about 21.5 pct S. For these points the ingoing gas mixtures ranged from 0.59 up to 100 pct H<sub>2</sub>S. Except for the points at highest percentage of H<sub>2</sub>S, the entrant and exit gases were brought to equality within 0.01 to 0.02 pct H<sub>2</sub>S without difficulty. Points 10 to 19 represent equilibria of the gas mixtures with two conjugate melts, Cu and Cu<sub>2</sub>S, respectively. During these ten determinations it was observed that the exit gas after once reaching the equilibrium value remained there regardless of small variations in the gas bubbled into the melt. Thus points 10, 11, and 12 represent checks of a single equilibrium condition, the exit gas remaining at 0.506 to 0.509 pct H<sub>2</sub>S while the ingoing gas was deliberately varied from 0.527 to 0.491 pct H<sub>2</sub>S. Points 14 and 15 show a similar check. These data illustrate the rapidity of reaction of the gas with the melt obtained by the bubbling technique. For all points except 30, 31, and 32 the percentage of H<sub>2</sub>S in the outgoing gas is taken as the equilibrium value. The failure to reach 100 pct H<sub>2</sub>S in the outgoing gas for points 30, 31, and 32 was associated with sulphur deposition in cold parts of the furnace tube and gas exit tubes, so for these points it was assumed that the equilibrium gas composition was that of the products of dissociation of pure H<sub>2</sub>S at furnace temperature and pressure.

In Table III the results are placed in a more convenient form for subsequent use. The corrected

Table III. Equilibrium Values of  $\frac{p_{H_2S}}{p_{H_2}}$  vs. Mol Fraction Sulphur at 1150°, 1250°, and 1350°C

| Point No.           | S, Wt Pct* | Mol Fraction S (N <sub>s</sub> ) | $\frac{p_{H_2S}}{p_{H_2}} \times 100^\dagger$ |
|---------------------|------------|----------------------------------|-----------------------------------------------|
| Temperature, 1150°C |            |                                  |                                               |
| 14†                 | 19.76      | 0.3281                           | 0.353                                         |
| 15†                 | 19.82      | 0.3289                           | 0.352                                         |
| 4                   | 20.01      | 0.3316                           | 0.677                                         |
| 3                   | 20.09      | 0.3327                           | 1.056                                         |
| 25                  | 20.11      | 0.3329                           | 1.549                                         |
| 26                  | 20.26      | 0.3350                           | 3.17                                          |
| 27                  | 20.46      | 0.3378                           | 12.82                                         |
| 31                  | 21.43      | 0.3533                           | 190.0                                         |
| Temperature, 1250°C |            |                                  |                                               |
| 10†                 |            |                                  | 0.498                                         |
| 11†                 | 19.54      | 0.3250                           | 0.501                                         |
| 12†                 | 19.54      | 0.3252                           | 0.497                                         |
| 17†                 | 19.60      | 0.3259                           | 0.484                                         |
| 9                   | 19.65      | 0.3266                           | 0.586                                         |
| 24                  | 19.99      | 0.3313                           | 1.166                                         |
| 8                   | 20.04      | 0.3317                           | 1.055                                         |
| 23                  | 20.06      | 0.3322                           | 2.04                                          |
| 2                   | 20.12      | 0.3331                           | 1.72                                          |
| 5                   | 20.20      | 0.3342                           | 3.01                                          |
| 7                   | 20.27      | 0.3352                           | 2.59                                          |
| 6                   | 20.32      | 0.3359                           | 2.83                                          |
| 28                  | 20.48      | 0.3381                           | 12.23                                         |
| 32                  | 21.54      | 0.3528                           | 131.0                                         |
| Temperature, 1350°C |            |                                  |                                               |
| 13†                 | 19.42      | 0.3236                           | 0.636                                         |
| 19†                 | 19.61      | 0.3260                           | 0.616                                         |
| 20                  | 19.56      | 0.3253                           | 0.876                                         |
| 21                  | 19.66      | 0.3267                           | 1.032                                         |
| 22                  | 20.05      | 0.3319                           | 2.00                                          |
| 29                  | 20.52      | 0.3387                           | 12.20                                         |
| 30                  | 21.39      | 0.3500                           | 89.7                                          |

\* Corrected pct S calculated from chemical analysis:

$$\text{Corr. Pct S} = \frac{\text{Pct S}}{\text{Pct S} + \text{Pct Cu}} \times 100$$

† Corrected for dissociation and corrected from actual experimental temperature to 1150°, 1250°, or 1350°C.

‡ Two liquid phases in equilibrium.

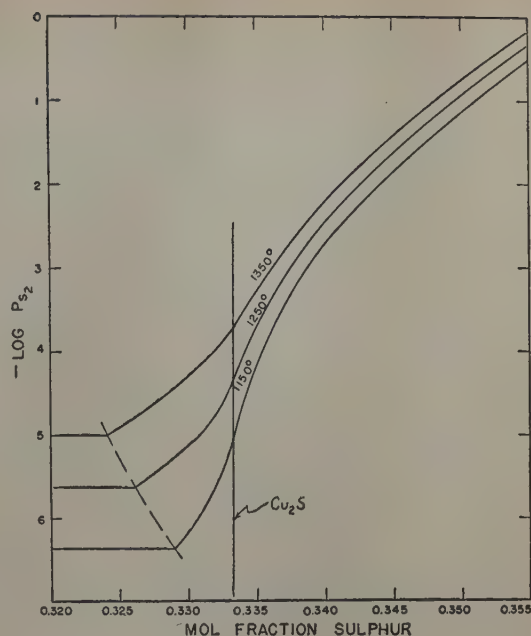


Fig. 4—Variation of sulphur pressure with mol fraction sulphur at 1150°, 1250°, and 1350°C.

values of  $p_{H_2S}/p_{H_2}$  were found as follows: First, the H<sub>2</sub>S:H<sub>2</sub> ratio in the outgoing gas, as found by analysis, was corrected for dissociation of H<sub>2</sub>S into H<sub>2</sub> and S<sub>2</sub> at the furnace temperature, using Kelley's free-energy equation for the dissociation reaction. Then preliminary plots of the data were made to estimate the rate of change of  $p_{H_2S}/p_{H_2}$  with temperature at the various compositions. These estimated temperature coefficients then were used to correct the values of  $p_{H_2S}/p_{H_2}$  from the odd measured temperatures to the even temperatures 1150°, 1250°, and 1350°C.

Fig. 3 shows the relations of  $\log p_{H_2S}/p_{H_2}$  to mol fraction S at 1150°, 1250°, and 1350°, and was plotted from the data in Table III. The horizontal lines at the left correspond to the H<sub>2</sub>S:H<sub>2</sub> ratio determined with both Cu and Cu<sub>2</sub>S phases present in the system, and these lines intersect the experimental curves at values of mol fraction S which represents the compositions of Cu-saturated sulphide melts. Several of the points plotted in Fig. 3 show rather larger deviations for the curves than might be desired. In this connection it should be noted that the scale of the abscissa is a rather expanded scale, the whole range from  $N_s = 0.320$  to  $N_s = 0.355$  corresponding to a range in S content of only 2.5 wt pct, from 19.2 to 21.7 pct S. This composition range is considerably smaller than was anticipated from previous work.<sup>3</sup> Accordingly, the scatter in Fig. 3 results chiefly from small errors in the melt analyses. In drawing the smooth curves in the vicinity of the Cu<sub>2</sub>S composition, the following matters were considered: 1—The solid solubility of Cu in Cu<sub>2</sub>S is small, so that the presence or absence of metallic Cu in the solid samples (determined by microscopic examination) was used as a supplementary guide in checking the analyses of samples near Cu<sub>2</sub>S in composition.<sup>4</sup> 2—The curves probably should not inflect at the composition Cu<sub>2</sub>S. 3—If the curves intersect at all, all three should do so at a common point to avoid the improbable finding that the partial molal heat of solution of S in the melt varies sharply with temperature.

Fig. 4 shows the relations of  $p_{S_2}$  to composition for the three experimental temperatures. These curves were calculated to correspond to the smoothed curves of Fig. 3, using Kelley's<sup>6</sup> free-energy equation for the dissociation of  $H_2S$  to calculate equilibrium values of  $p_{S_2}$  corresponding to the measured values of  $p_{H_2S}/p_{H_2}$ . Kelley's data for this equilibrium are represented accurately in the temperature range of this investigation by the relation:

$$\log p_{S_2} = 2 \log \left( \frac{p_{H_2S}}{p_{H_2}} \right) - \frac{9665}{T} + 5.342$$

The plot in Fig. 4 shows the very steep variation of sulphur pressure with composition,  $p_{S_2}$  increasing from the vicinity of  $10^{-6}$  and  $10^{-5}$  atm for liquids below  $Cu_2S$  in sulphur content to nearly 1 atm for liquids containing a small excess of S over  $Cu_2S$ .

In view of the steep variation of sulphur pressure with sulphur content and in view of the accompanying experimental uncertainties in sulphur analyses, the data do not permit accurate determinations of the heat of solution of sulphur in the melts from the variation of sulphur activity with temperature at constant composition. However, on the basis of the smoothed data as represented by the curves in Fig. 3, the partial molal heat content of sulphur in the melt relative to  $H_2S$  gas increases from about -28,000 cal per g-atom S in Cu-saturated melts to about -12,000 cal for  $Cu_2S$  and then increases further to about +12,000 cal for the highest S melts. The corresponding estimates for the differential heat of solution of  $S_2$  gas in the melts are -100,000 cal per g mol  $S_2$  in Cu-saturated melts, -68,000 cal per g mol in  $Cu_2S$ , and -20,000 cal per g mol in the melts having sulphur pressures approaching an atmosphere (21.5 pct S).

**Sulphur Activities and Compositions of Cu-Saturated Liquids:** Fig. 5 shows the relationship of log

$$\frac{p_{H_2S}}{p_{H_2}} \text{ to } \frac{10^4}{T} \text{ for equilibrium determinations 10}$$

through 19 in which two liquid phases,  $Cu_2S$  and Cu, were present at equilibrium in the crucible. The experimental points fall on a straight line within experimental error, following the relation:

$$\log \frac{H_2S}{H_2} = -\frac{2920}{T} - 0.394$$

Also plotted in Fig. 5 are the data of Cox and co-

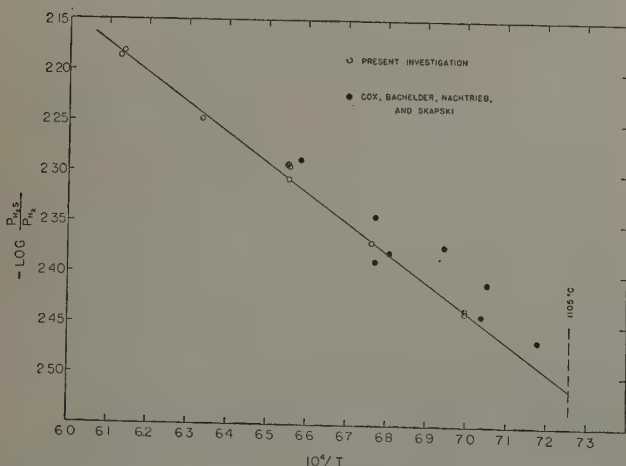


Fig. 5—Relation of  $\log p_{H_2S}/p_{H_2}$  to  $1/T$  for Cu-saturated melts.

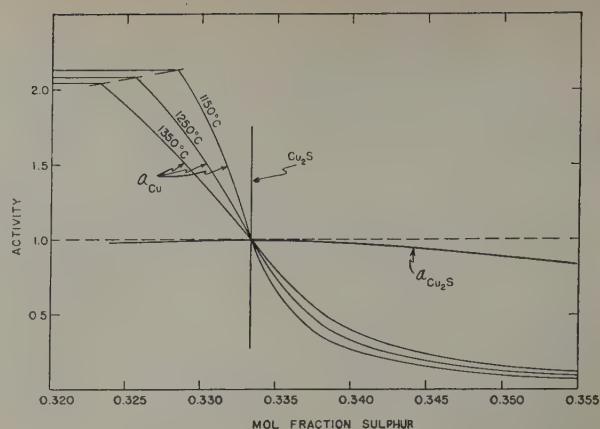


Fig. 6—Activities of Cu and  $Cu_2S$  calculated by Gibbs-Duhem integration.

workers,<sup>7</sup> which check the new data reasonably well. Combination of the above equation with the rela-

tion of  $p_{S_2}$  to  $\frac{p_{H_2S}}{p_{H_2}}$  and  $T$  derived from Kelley's data

gives the relation of  $p_{S_2}$  to  $T$  for Cu-saturated melts:

$$\log p_{S_2} = -\frac{15,505}{T} + 4.56$$

The mol fractions of S ( $N_s$ ) corresponding to Cu saturation can be read from Fig. 3 at the intersections of the horizontal lines giving  $\log \frac{p_{H_2S}}{p_{H_2}}$  for the systems containing two liquid phases with the curves for sulphide melts of varying composition. Table IV gives the results of these determinations and includes also the recent determination by Jensen<sup>4</sup> at 1105°C, which checks well with the results of the present investigation. As mentioned previously, the various determinations of the compositions of Cu-saturated mattes reported in the literature have been somewhat discordant, some of the earlier work indicating a composition range from Cu-saturation to  $Cu_2S$  as much as five times the range in percent S (e.g., 19.4 to 20.14 pct S at 1350°C) found in the present investigation. When the various experimental methods are considered, the authors feel that the data in Table IV represent the most reliable information on the compositions of Cu-saturated sulphide melts.

**Activities of Cu and  $Cu_2S$ :** Using the Gibbs-Duhem integration,<sup>10</sup> copper activities can be calculated from the relationship of sulphur activity (measured by  $p_{H_2S}/p_{H_2}$ ) to mol fraction S ( $N_s$ ). That is, at constant temperature:

$$\log a_{Cu} = -\int \frac{N_s}{1-N_s} d \log \frac{H_2S}{H_2}$$

In evaluating this integral, it is necessary to select as a limit the standard state for copper in which  $a_{Cu} = 1$ . It would be desirable to use pure liquid Cu as the standard state, but the data are not yet available to carry the above integration to this limit on the liquid-Cu side of the Cu-S system. Accordingly, the standard state for copper was arbitrarily chosen as the solution of composition corresponding exactly to  $Cu_2S$ , for which  $N_s = 1/3$ . Results of the integration based on the experimental data are plotted in Fig. 6. It can be seen that the activity of



Cu in liquid  $\text{Cu}_2\text{S}$  is roughly half the activity of Cu in a liquid-Cu-saturated melt, and, therefore, is a little less than half the activity of pure liquid Cu. In general, also, the activity of copper decreases rather sharply with increasing sulphur content, as would be expected from the rapid increase in sulphur pressure.

The gas-melt equilibria can be considered in terms of the reaction:



for which the equilibrium constant is:

$$k = \frac{p_{\text{H}_2\text{S}} a_{\text{Cu}}^2}{p_{\text{H}_2} a_{\text{Cu}_2\text{S}}}$$

If the standard states for both Cu and  $\text{Cu}_2\text{S}$  are taken as the solution of composition  $\text{Cu}_2\text{S}$ , the equilibrium constant at any temperature becomes equal to  $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$  at the composition  $\text{Cu}_2\text{S}$  and can be evaluated from the experimental data, giving:

$$\log k = -\frac{2630}{T} + 0.059$$

The corresponding equation for the standard free-energy change in the reaction is:

$$\Delta F^\circ = 12,000 - 0.27T$$

It should be kept in mind that this free-energy equation is valid only for the standard states of Cu

Table IV. Compositions of Cu-Saturated Copper Sulphide

| Temperature, °C | Mol Fraction S | S, Wt Pct | $\text{Cu}_2\text{S}$ , Wt Pct |
|-----------------|----------------|-----------|--------------------------------|
| 1350            | 0.323          | 19.4      | 96.3                           |
| 1250            | 0.325          | 19.6      | 97.0                           |
| 1150            | 0.329          | 19.8      | 98.4                           |
| 1105*           |                | 19.79     |                                |

\* From Jensen.<sup>4</sup>

and  $\text{Cu}_2\text{S}$  for which the equation is derived and thus should not be compared directly with other free-energy equations for the same reaction but based on different standard states.

Activities of  $\text{Cu}_2\text{S}$  for various compositions of liquid sulphides at various temperatures can be calculated by substituting  $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$  and  $a_{\text{Cu}}$  (from the Duhem integration) into the equilibrium constant and then solving for  $a_{\text{Cu}_2\text{S}}$ . Results of these calculations are plotted in Fig. 6. One curve shows the results of the calculations adequately over the entire temperature range 1150° to 1350°C of the present investigation.

### Summary

The activity of sulphur in liquid copper sulphide, from compositions corresponding to saturation with copper to compositions approaching 1 atm in sulphur pressure, was measured over the temperature range 1150° to 1350°C. The experiments consisted in finding for each melt composition and temperature the ratio  $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$  in a gas mixture at equilibrium with the melt. Equilibrium was established by bubbling the gas mixture through the liquid and adjusting the gas composition until no reaction occurred, as shown by comparison of the  $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$  ratio in entrant and exit gases. The equilibrium partial pressures of  $\text{S}_2$  gas were calculated from the  $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$  data, using Kelley's free-energy equation for the dissociation of  $\text{H}_2\text{S}$ .

The sulphur pressures ( $p_{\text{S}_2}$ ) of liquid copper sulphides were found to be very sensitive to composition, especially as the S contents were increased beyond  $\text{Cu}_2\text{S}$ . At 1150°C,  $p_{\text{S}_2}$  was found to be  $4.6 \times 10^{-7}$  atm for Cu-saturated melt,  $9.4 \times 10^{-6}$  atm for  $\text{Cu}_2\text{S}$  (20.14 pct S), and 0.14 atm for the 21.5 pct S melt. The corresponding figures at 1250°C were  $2.4 \times 10^{-6}$ ,  $4.6 \times 10^{-5}$ , and 0.23 atm, respectively, and at 1350°C were  $10^{-5}$ ,  $1.8 \times 10^{-4}$ , and 0.35 atm, respectively. The large increase in  $p_{\text{S}_2}$  for slight increases in S above  $\text{Cu}_2\text{S}$  accounts for the well-known fact that artificial preparations of  $\text{Cu}_2\text{S}$  involving melting in open containers always give products close to  $\text{Cu}_2\text{S}$  in composition.

The sulphur pressures ( $p_{\text{S}_2}$ ) of liquid copper sulphides increase with increasing temperature, this increase being more marked for liquids below  $\text{Cu}_2\text{S}$  in sulphur content. From the variations of  $p_{\text{S}_2}$  with temperature, the partial molal heats of solution of  $\text{S}_2$  were estimated to be approximately -100,000 cal per mol for Cu-saturated melts, -68,000 cal per mol for  $\text{Cu}_2\text{S}$  (20.14 pct S), and -20,000 cal per mol for melts with 21.5 pct S.

The equilibrium measurements for the systems containing the two conjugate solutions, liquid Cu and liquid  $\text{Cu}_2\text{S}$ , are represented by the following equation:

$$\log \frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}} = -\frac{2920}{T} - 0.394$$

The corresponding equation for the sulphur pressure of the two-phase system is as follows:

$$\log p_{\text{S}_2} = -\frac{15,505}{T} + 4.56$$

The sulphur contents of the liquid copper sulphides saturated with copper were found to be 19.8 pct at 1150°C, 19.6 pct at 1250°C, and 19.4 pct at 1350°C. These results are concordant with Jensen's recent determination of 19.79 pct at 1105°C but disagree with earlier data which indicated a much larger solubility of Cu in  $\text{Cu}_2\text{S}$ .

### Acknowledgments

The authors wish to express their appreciation to the International Nickel Co. for their support of this work by fellowship awards for the period 1947 to 1949. Also, the authors wish to acknowledge the assistance of L. M. Baker in making the chemical analyses.

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# Microscopic Observation of the Solidification Of Cu-Ni Alloy Droplets

by R. E. Cech and D. Turnbull

THE supercooling behavior of pure liquid metal droplets has been described.<sup>1</sup> The solidification behavior of small droplets of Cu-Ni alloys as a function of composition is described herein. The Cu-Ni system is of interest for such an investigation because the components are miscible in all proportions in both the liquid and solid state and the phase diagram of the system, Fig. 1, is a type often encountered in metal systems.

It was noted by Van Riemsdyk<sup>2</sup> and others that the nature of the "blick" of gold droplets during assaying is not perceptibly affected by the content of the platinum group metals that are soluble in both liquid and solid gold. With the exception of these very qualitative observations there appear to have been no prior investigations of the supercooling of alloy droplets.

A series of nine alloys varying in composition by 10 pct (nominal weight) steps was made using certified OFHC copper, 99.996 pct purity, obtained from the American Brass Co., and electrolytic nickel pellets, 99.92 pct purity, obtained from the International Nickel Co. The alloys were melted and cast in vacuo in a high frequency induction furnace. Segregation was minimized by chill casting into 1-in. diam steel molds. Each alloy rod was homogenized at a temperature 50°C lower than the solidus for 100 hr in dry hydrogen. Samples for solidification experiments and chemical analysis were machined from the same portion of each rod and at a depth of 1/4 in. from the rod surface. A Carboloy tool was used in taking turnings to minimize contamination of sample by the cutting tool. As a

check, a number of samples for microscopic observation were chipped from the ingot with a fragment of pyrex glass. The resultant data in all cases agreed, within experimental error, with the data obtained from machined turnings.

A number of small particles, 30 to 50 micron diam, of a Cu-Ni alloy were placed in a quartz vial 1/32 in. diam x 1/4 in. long. This was inserted into a platinum ribbon heater and mounted in a high temperature microscope stage. The general procedure followed in inserting samples into the stage and measuring the temperature of melting and solidification was the same as described in an earlier paper.<sup>1</sup> A chromel-alumel thermocouple was used to study alloys of 88.93 pct Cu, 80.62 pct Cu, and 72.27 pct Cu. A platinum-10 pct rhodium thermocouple was used for the remainder of the alloys.

## Procedure

The assembled high temperature microscope stage was first evacuated and the sample given a 2 min in situ treatment at 900°C in dry hydrogen to remove surface oxides which might otherwise catalyze crystal nucleation. After this treatment the atmosphere was changed to purified helium and melting and solidification were observed microscopically. It was not possible to determine the solidus with certainty. However, the liquidus temperature was measured very accurately since the surface of the particle changed in appearance from coarse and uneven to smooth, mirror-like within a few degrees. The visually determined liquidus temperature was checked by finding the highest temperature to which the particle could be heated such that it did not supercool upon lowering the temperature. This temperature which checked within experimental error with that found by observing surface change was assumed to be characteristic of the thermodynamic liquidus. In order to minimize the effect of selective evaporation of copper from the alloy, samples were changed frequently and the droplets were heated no more than 50°C in excess of the liquidus temperature  $T_1$ . When the latter conditions were fulfilled,  $T_1$  values were reproducible.

After melting, the temperature was decreased slowly until the particles solidified. The sudden release of heat of fusion on solidification caused the

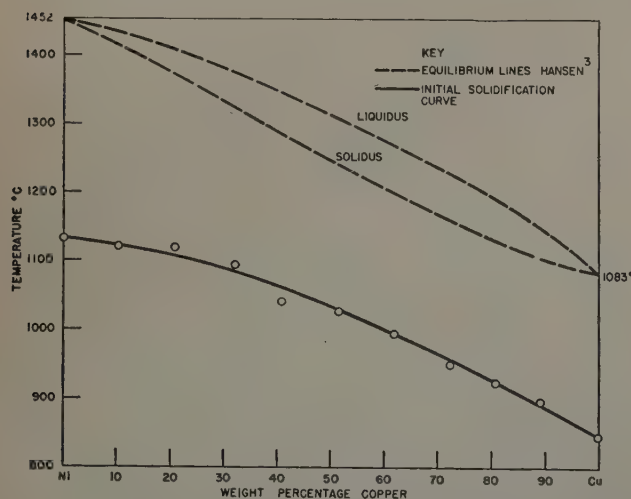


Fig. 1—Solidification temperatures of Cu-Ni alloys as a function of composition.

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supercooled particles to blink, or recalesce. Also, at the same instant, the particle surface could be observed to change from mirror-like to a dendritic type pattern. It was necessary, when observing the higher melting, Ni-rich alloys to use filters to decrease radiation intensity.

## Results

The alloy compositions and results are summarized in Table I and plotted on the constitution diagram of Fig. 1. The  $(\Delta T_-)_{\max}$  values listed for pure copper and nickel were taken from the previous investigation of pure metals.<sup>1</sup> The values of  $(\Delta T_-)_{\max}$  for the alloys are the average of several determinations on a number of samples but the maximum deviation observed in any determination was within 2 pct of the average.

In agreement with earlier observations on pure metals the frequency of supercooling to  $(\Delta T_-)_{\max}$  was much less in the absence of a flux. It is probable that the pyrex flux combined with nucleation catalysts that may have been picked up from the alundum crucibles used in making the alloys. When a pyrex flux was used the particles supercooled to  $(\Delta T_-)_{\max}$  consistently.

Occasionally, a surface oxide coating that nucleated solidification at  $\Delta T_- < (\Delta T_-)_{\max}$  formed on the alloys of 88.93 pct Cu and 80.62 pct Cu in a helium atmosphere. Therefore, a hydrogen atmosphere was used for these alloys. The ratio  $\Delta T_{-\max}/T_1$  for results obtained in hydrogen agree very well with the ratios for the other alloys of the system.

The metal droplets after solidification displayed a dendritic surface structure. A micrograph of a supercooled droplet of 80.62 pct Cu in cross-section (Fig. 2) illustrates the dendritic structure formed during solidification. It was also apparent that the solidified particle was a single crystal as might be expected in view of the rapid crystal growth rate. The dendritic segregation may indicate that at least a portion of the droplet had been heated to the equilibrium freezing temperature before solidifying. Neglecting heat losses to the surroundings, the latent heat of fusion released by the solidification of approximately 60 pct of the droplet is sufficient to heat the entire droplet to the equilibrium temperature. It is therefore apparent that segregation during solidification may occur in a supercooled alloy droplet as well as in bulk solidification.

The initial solidification temperatures are more properly defined as temperatures at which the frequency of nucleus formation becomes very great. It is known that the temperature dependence of nucleation rates in tin<sup>4</sup> and mercury<sup>5</sup> is so great that



Fig. 2—Cross-section of 80.62 pct Cu alloy droplet supercooled to  $\Delta T_{-\max}$  before solidification. X500.

even large variations in speed of cooling will have no perceptible effect, in these experiments, on the temperature of initial solidification. To extend the knowledge of temperature dependence of nucleation rate to alloys in a qualitative way, a number of 50 micron particles of 40.89 pct Cu were first melted and then cooled to a temperature 20°C above  $(\Delta T_-)_{\max}$  and held 30 min. Upon further cooling they were found to solidify at  $(\Delta T_-)_{\max}$  thus indicating that the prolonged hold at the higher temperature had no measurable effect on the temperature of subsequent solidification.

## Summary

The solidification behavior of Cu-Ni alloy droplets was studied as a function of composition by means of a high temperature microscopic technique described previously.<sup>1</sup> The ratio of the amount of supercooling  $(\Delta T_-)_{\max}$  to the absolute liquidus temperature was found to be  $0.18 \pm 0.01$ , see Table I, which checks closely the value of  $0.18 \pm 0.02$  for the ratio of  $(\Delta T_-)_{\max}$  to the absolute melting temperature found for pure metals.

A cross-section of a supercooled particle displayed segregation indicating that the heat of fusion was probably sufficient to raise the droplet to the equilibrium freezing temperature and allow a portion of the particle to solidify by normal dendritic growth.

It was demonstrated that the temperature dependence of the nucleation rate was about as large as for pure metals.

## Acknowledgment

The authors are pleased to acknowledge the assistance of Mrs. Joyce Rowland in much of the experimental work reported in this paper.

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Table I. Alloy Compositions

| Alloy Composition<br>Cu, Wt Pct* | Liquidus Temperature,<br>°K ( $T_1$ ) | Maximum Supercooling<br>( $\Delta T_-)_{\max}$ | ( $\Delta T_-)_{\max}$<br>( $T_1$ ) |
|----------------------------------|---------------------------------------|------------------------------------------------|-------------------------------------|
| 100.00                           | 1356 (melting point)                  | 236                                            | 0.174                               |
| 88.93                            | 1418                                  | 254                                            | 0.179                               |
| 80.62                            | 1466                                  | 268                                            | 0.183                               |
| 72.27                            | 1511                                  | 278                                            | 0.184                               |
| 61.95                            | 1548                                  | 275                                            | 0.178                               |
| 51.51                            | 1585                                  | 281                                            | 0.177                               |
| 40.89                            | 1618                                  | 304                                            | 0.188                               |
| 32.01                            | 1653                                  | 280                                            | 0.169                               |
| 20.39                            | 1683                                  | 289                                            | 0.172                               |
| 10.28                            | 1707                                  | 314                                            | 0.184                               |
| 0.00                             | 1725 (melting point)                  | 319                                            | 0.185                               |

\* Balance nickel.

# Solubility of Hydrogen in Molten Lead

by W. R. Opie and N. J. Grant

THE amount of hydrogen that will dissolve in lead has been considered negligible. However, a limited number of measurements made recently using apparatus built for determining hydrogen solubility in aluminum alloys<sup>1</sup> indicate that liquid lead will hold a small but appreciable amount of hydrogen in solution. The apparatus used was similar to that developed by Sieverts.<sup>2</sup> This consists of a bulb to hold the molten metal, a gas burette for introducing a measured quantity of gas into the bulb and a manometer for measuring the gas pressure in the bulb. Measurements are made by introducing enough of an insoluble gas (helium) to fill the system at a given temperature and pressure, thereby determining the hot volume of the bulb. This gas then is pumped out and hydrogen is introduced until the same pressure is reached, the metal being maintained at the same temperature while in contact with each gas. The difference between the volumes corrected for pressure is then the hydrogen solubility. A more detailed account of the procedure can be found in refs. 1 and 2.

The lead was melted in an alundum crucible by induction heating to provide uniform temperature and an important stirring effect. The metal was the purest obtainable, 99.999+, prepared especially by the research department of the American Smelting

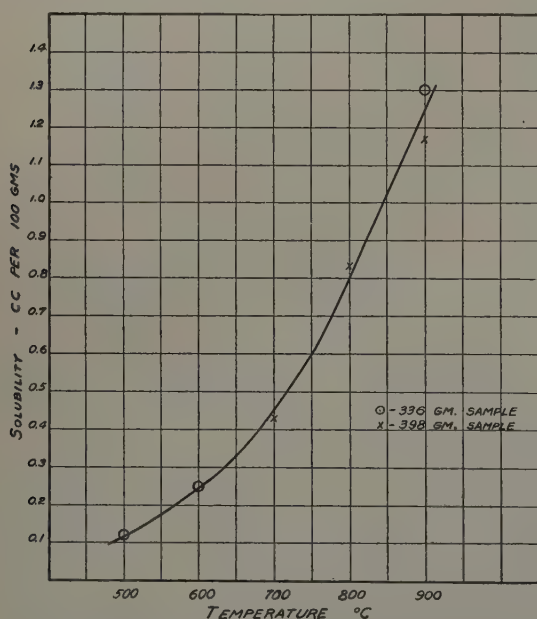


Fig. 1—Effect of temperature upon the solubility of hydrogen in molten lead at 760 mm Hg.

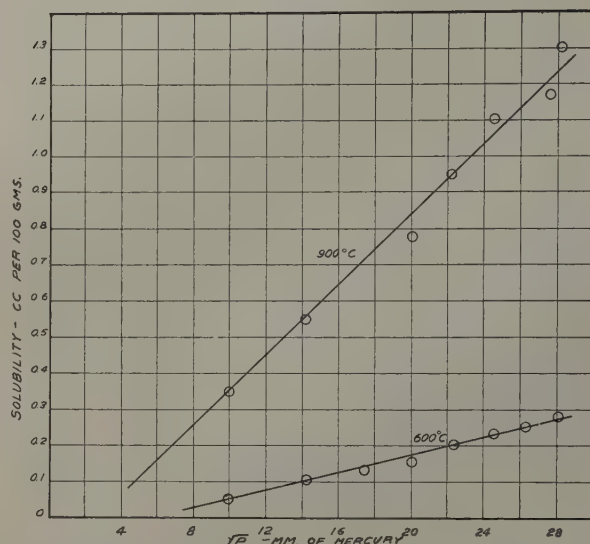


Fig. 2—Effect of pressure upon the solubility of hydrogen in molten lead.

and Refining Co. Measurements were made by approaching the equilibrium value from high and low temperatures during the constant pressure runs, and from high and low pressures when the temperature was held constant. Thus a number of measurements were made on each of two large samples which weighed 336 and 398 g. The gases were purified as described in ref. 1.

The effect of temperature on the solubility was studied with the pressure held constant at 760 mm of Hg. To show the effect of pressure, solubility measurements were taken at two constant temperatures, 600° and 900°C.

## Results

The effect of temperature on hydrogen solubility is shown in Fig. 1. The curve representing the data is parabolic, as are plots of hydrogen solubility vs. temperature for other metals and alloys (aluminum,<sup>1</sup> copper,<sup>3</sup> and iron,<sup>4</sup> for example). Fig. 2 shows the relationship that exists when the solubility is

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plotted against the square root of the pressure. As can be seen from this plot, the Sieverts' relationship, "solubility of a diatomic gas varies as the square root of the pressure if the temperature remains constant," can be applied to lead. The fact that the lines relating the solubility to the square root of the pressure do not quite pass through the origin indicates that the values are slightly low. This can be explained primarily by the difference in heat conductivity between hydrogen and helium but also by the small values of solubility being measured. Hydrogen, being a better conductor than helium, would heat the surrounding bulb glassware above the metal to a slightly higher temperature than would the helium. Because the space in the system occupied by the gas is hotter when hydrogen is in contact with the metal, the net result is that less hydrogen than helium for a given pressure is needed to fill this space. This effect is very much more pronounced when a gas with even lower heat conductivity, such as argon, is used as the inert gas, as was observed in several trial runs.

When the equilibrium constant  $\log_{10}$  for the solubility equation:



determined by expressing the solubility as the mol fraction, is plotted against the reciprocal of the absolute temperature, the heat of solution can be calculated from the slope of the line using the Van't Hoff equation:

$$\log_{10} K = \frac{-\Delta H}{0.575 T} + C$$

Fig. 3 is such a plot with the solubility, ( $\log_{10}$ ) expressed in cc of hydrogen per 100 g of lead, and the equilibrium constant ( $\log_{10}$ ) both plotted against the reciprocal absolute temperature. From this plot the solubility may be expressed as:

$$\log_{10} S = \frac{-2450}{T} + 2.19$$

The total heat of solution, including the heat of dissociation of diatomic to monatomic hydrogen and the heat of solution of the monatomic hydrogen, has

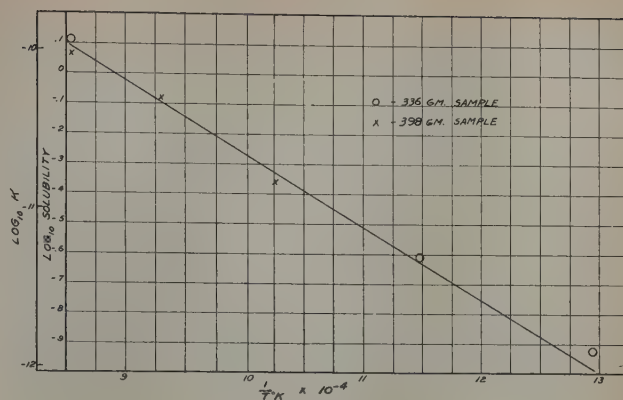


Fig. 3—Van't Hoff plot of solubility data.

been determined from the slope to be 22,300 cal per mol of diatomic hydrogen.

### Conclusions

1—The solubility of hydrogen in molten lead may be expressed by the equation:

$$\log_{10} S = \frac{-2450}{T} + 2.19$$

2—Sieverts' law is obeyed within the temperature and pressure ranges investigated.

3—The heat of solution of hydrogen in lead is 22,300 cal per mol of diatomic hydrogen.

### Acknowledgment

The authors wish to thank Edith Weiser for her assistance in obtaining the results. The work was sponsored by the Bureau of Aeronautics.

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### Technical Note

## Surface Diffusion in Sintering of Spheres on Planes

by P. Schwed

IN determining the mechanism responsible for sintering, the most direct procedure available is the comparison of the observed time and temperature dependence of the process with the dependence to be expected upon the basis of each conceivable mechanism. This was done by Kuczynski<sup>1</sup> who, in treating the mechanism of surface diffusion, postulated, in effect, that the concentration gradient of vacancies is different from zero only within the

neck. This procedure was recently questioned by Cabrera<sup>2</sup> who assumed, on the contrary, that diffusion occurs only in the region outside the neck. In the present note, the calculations are performed without restriction on the region of diffusion.

To carry out this objective it is first necessary to

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review briefly Cabrera's approach. He divided the surface of the sphere being sintered into two parts: 1—A flat portion,  $AB$  in Fig. 1, with an essentially infinite radius of curvature; and 2—the neck,  $AA$  in Fig. 1, which at a given stage of the process has a radius of curvature,  $\rho$ . This difference in curvature leads to a higher concentration of vacancies in the neck with the result that diffusion of atoms occurs into the neck from the undisturbed part of the surface. It is assumed further that there exists a process, say condensation, which replaces the atoms lost from the flat part of the surface; and the equation of continuity is solved for this region of the surface under the assumption that diffusion and condensation balance (time independence) and with the boundary condition that the concentration of atoms at the junction,  $A$ , between the neck and the flat surface is that appropriate to the neck. The current at the junction then is calculated, and from the current the law of growth of the neck may be found.

This approach suffers from the difficulty that the equation of continuity does not hold throughout the surface, since the current of atoms is discontinuous across the boundary. This follows from the fact that the concentration of atoms in the neck is taken as constant so that the current of atoms within the neck is everywhere zero, according to the diffusion equation. The inconsistency here arises from a failure to consider in proper detail the situation at the surface of the neck. The most direct way of doing this is to apply the same principles to calculating the concentration in the neck as were employed for the flat surface. This means that the process which supplies the atoms lost by the flat region removes the excess atoms in the neck, for instance by evaporation.

Revising Cabrera's notation slightly, let  $n_1$  be the concentration of adsorbed atoms in the flat region and  $n_2$ , that in the neck; further, let  $y$  be a coordinate measured from the junction  $A$  with a positive direction away from the neck and  $y_s = (D_s t_s)^{1/2}$  where  $D_s$  is the coefficient of surface diffusion and  $t_s$  is the relaxation time for condensation. Then, if  $n(\infty)$  and  $n(\rho)$  are the equilibrium concentrations of adsorbed atoms in the flat surface and neck, respectively, the appropriate equations are (cf. ref. 2, eq 3):

$$\frac{d^2}{dy^2} [n(\infty) - n_1] = \frac{n(\infty) - n_1}{y_s^2} \quad [1]$$

and

$$\frac{d^2}{dy^2} [n(\rho) - n_2] = \frac{n(\rho) - n_2}{y_s^2} \quad [2]$$

Eq 2 is based upon the assumption that diffusion occurs along the curved surface of the neck in essentially the same fashion as on a plane surface of the same length. The following boundary conditions apply:

$$\begin{aligned} n_1 &= 0 \text{ at } y = \infty \\ n_1 &= n_2 \text{ at } y = 0 \end{aligned}$$

$$\frac{dn_1}{dy} = \frac{dn_2}{dy} \text{ at } y = 0 \quad [3]$$

$$\frac{dn_2}{dy} = 0 \text{ at } y = y_0 = -\frac{\pi\rho}{2} \text{ (center of neck)}$$

where  $y_0$  is the coordinate of the center of the neck.

The last two follow respectively from the equality of currents at the junction  $A$  and the vanishing of the current at the center  $C$ , of the neck on account

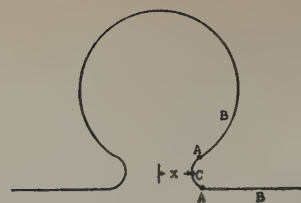


Fig. 1—Typical sphere.

of symmetry. The solution of eqs 1 and 2 subject to the conditions of eq 3 is:

$$\begin{aligned} n(\infty) - n_1 &= \frac{n(\infty) - n(\rho)}{2} (1 - e^{\frac{2y_0}{y_s}}) e^{-\frac{y}{y_s}} \\ n(\rho) - n_2 &= \left[ \frac{n(\infty) - n(\rho)}{2} \right] (e^{\frac{y}{y_s}} + e^{-\frac{y+2y_0}{y_s}}) \end{aligned} \quad [4]$$

The current  $J_s$  through the junction  $A$  is therefore:

$$\begin{aligned} J_s &= \frac{n(\infty) - n(\rho)}{2} \frac{D_s}{y_s} (1 - e^{\frac{2y_0}{y_s}}) \\ &= \frac{n(\infty) - n(\rho)}{2} \frac{D_s}{y_s} (1 - e^{-\frac{\pi\rho}{y_s}}) \end{aligned} \quad [5]$$

In interpreting eq 5, it is necessary to exercise caution. If the process balancing diffusion is literally condensation or evaporation, the current found leads to no net growth since the atoms entering the neck are evaporated forthwith. If, however, the alternative suggestion of Cabrera's is followed, that the interchanges implied are between atoms in the kinks on the surface and normal surface atoms, the observed build-up of the surface of the neck occurs since the atoms entering the neck remain there. Assuming the latter process to be correct, eq 5 may be used to find the rate of sintering. For

$$\rho \ll \frac{y_s}{\pi}, 1 - e^{-\frac{\pi\rho}{y_s}} \text{ is nearly equal to } \frac{\pi\rho}{y_s}, \text{ and,}$$

because  $n(\infty) - n(\rho)$  varies as  $\frac{1}{\rho}$ ,  $J_s$ , as given by eq 5, is independent of  $\rho$  and the law of growth of the neck is  $x^3 \sim At$  where  $2x$  is the neck diameter.

On the other hand, for  $\rho \gg \frac{y_s}{\pi}$ , the law of growth is  $x^5 \sim At$  and is the same as for volume diffusion. It follows that on the present theory it is possible to distinguish surface diffusion from volume diffusion by experiments on small particles.

To expedite comparison of the three calculations a brief table giving the results of each of these is as follows:

|                        | $\rho \ll \frac{y_s}{\pi}$ | $\rho \gg \frac{y_s}{\pi}$ |
|------------------------|----------------------------|----------------------------|
| Kuczynski <sup>1</sup> | $x^3 \sim At$              | $x^3 \sim At$              |
| Cabrera <sup>2</sup>   | $x^5 \sim At$              | $x^5 \sim At$              |
| Eq 5                   | $x^3 \sim At$              | $x^5 \sim At$              |

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# Re-solution of Precipitated Silver in Copper-Silver Alloys

by Harold Margolin and Walter R. Hibbard, Jr.

**D**URING preliminary tests on the aging of a Cu-plus 5 pct Ag alloy,<sup>1</sup> a specimen which had been overaged 24 hr at 550°C was annealed in a nitrogen-hydrogen atmosphere first for 2 hr and then for an additional 28 hr at 600°C. After each anneal the specimen was cooled to room temperature in about ½ hr and X-ray photograms were made. The first film, Fig. 1a, revealed two sets of copper-base lines, one intense and corresponding to the parameter at 550°C, the other fainter and shifted away from the beam, corresponding to the larger parameter at 600°C (see arrows). The 30-hr film, Fig. 1b, revealed the same two sets of copper-base lines with a reversal of intensity. In neither case do the copper lines form a broad band which would be indicative of a range of compositions. This phenomenon is thus a "discontinuous" type of solution. A similar phenomenon was observed in a Ag-rich Cu-Ag alloy.<sup>2</sup> Finlay and Hibbard<sup>3</sup> have suggested that directional rather than random solution of precipitate occurs in some alloys.

Conceivably, for Cu-Ag alloys, the matrix-transition-precipitate precipitation sequence is reversible for the re-solution of the precipitate caused by rapidly raising the annealing temperature of an overaged specimen. A copper-base transition structure supersaturated with solute might be formed around the precipitate as it dissolves, thus obviating the necessity for a gradually changing solute composition of the matrix. The solute atoms then might be transferred rapidly and locally from the transition to the matrix phase in the proper amount and at the proper location to obtain directly the new ex-

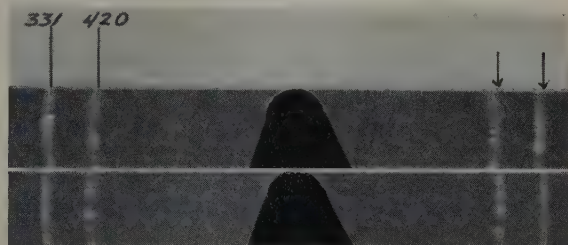


Fig. 1a (top)—Cu-Ag alloy aged 24 hr at 550°C, annealed 2 hr at 600°C.

Fig. 1b (bottom)—Same as Fig. 1a, but annealed 30 hr at 600°C.

panded solid solution. The theory implies a minimum of diffusion of solute in the matrix (i.e., no significant range of matrix composition) and possibly suggests that the composition of the transition structure will vary with the conditions of re-solution. A transition copper phase found in aged Cu-Ag alloys<sup>1</sup> might fulfill this function.

Evidence regarding this suggestion could be obtained in Cu-Ag alloys by overaging a specimen until no trace of the expanded copper lattice is present and then subjecting the specimen to a retrogression treatment. Re-appearance of the transition copper phase would confirm the theory. Additional details could be secured by varying both aging and retrogression temperatures.

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## Technical Note

# Fractographic Pattern for 475°C Embrittlement in Stainless Steel

by Carl A. Zapffe

**F**OR a number of years a puzzling phenomenon of brittleness in Class II ferritic stainless steels, developing in the temperature range near 475°C, has received increasing attention, but its nature remains essentially unknown. During an investigation of the fractographic structures in stainless steels, conducted in the author's laboratory the past several years, principally under sponsorship of the Office of

Naval Research, some observations of a new kind were found for "475°C embrittlement."

While the details of the study cannot be given here,<sup>1</sup> three fractographs will suffice to carry the

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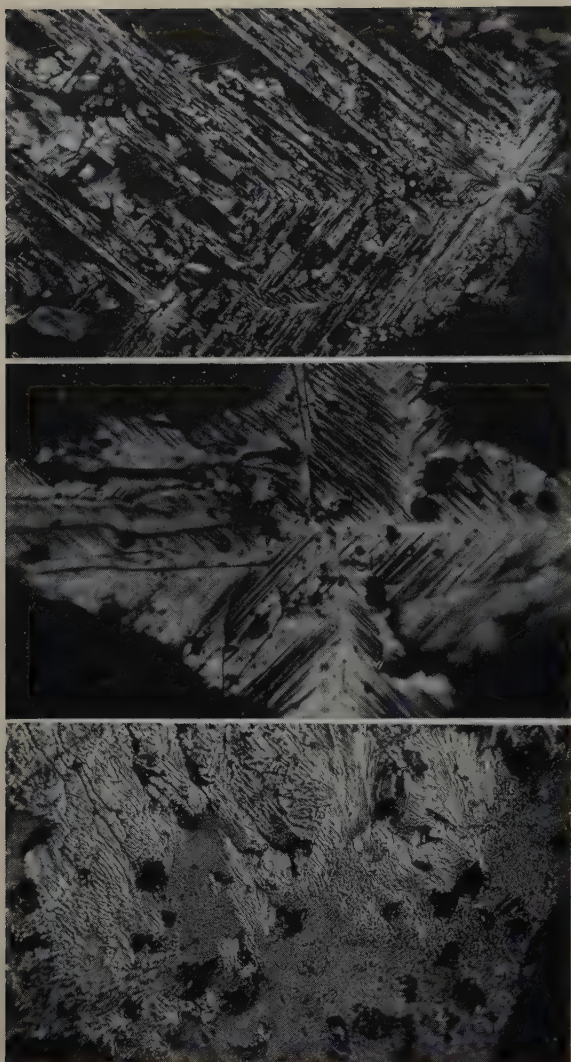


Fig. 1a (top)—Fractographic pattern for Type 446 stainless steel produced by rifle fire at 100°C, showing transgranular fracture typical for both embrittled and unembrittled metal at temperatures below the fractological change.

Fig. 1b (center)—Specimen fractured by rifle fire at 475°C. Still transgranular, the pattern expresses the fractological change, the crystallographic markings now representing slip rather than intersecting cleavages.

Fig. 1c (bottom)—Fractographic pattern believed to reveal a grain boundary precipitate and the phenomenon responsible for 475°C embrittlement.

Figs. 1a-1c: X850. Area reduced approximately 75 pct for reproduction.

point. These concern a sample of Type 446 stainless steel, held at 1150°C for 2½ hr, and slowly cooled in the furnace both to grow large grains and to expose the material to 475°C embrittlement as it passed through that range. Numerous other tests were conducted also, including some in which the specimens were held for 200 hr at temperatures within the embrittling range, but the results of all tests were similar.

In Fig. 1a a fractograph is shown for this steel fractured at 100°C by rifle fire from a 0.22-caliber bullet at a distance of 24 in. from the muzzle. The specimen was ¼-in. round bar containing a rectangular notch. The pattern discloses a sharp rec-

tangular symmetry of transgranular cleavage traverse on (001). Intersecting {100} cleavages are clearly evident. All visible angular relationships lie primarily at 90°, also at 45°.

This pattern is typical for *transgranular fracture* through this grade of steel whether fractured by hammer blow or by rifle fire over a wide range of temperature, and whether the metal has been embrittled or not by the phenomenon under discussion. No observable change in transgranular fracture pattern was caused by 475° embrittlement.

At temperatures above approximately 100°C, a fractological change manifests itself for specimens broken by hammer blow,<sup>2</sup> elastic responses being preceded by important plastic deformation with consequent obscuration of the fractographic pattern. By means of the higher velocity of rifle fire, the temperature of this fractological change is shifted upwards, such that a certain proportion of observable transgranular facets persists even at 475°C. One of these is shown in Fig. 1b. It will be noted that the pattern remains relatively flat, but that few if any of the block-like markings are in evidence. The parallel traces in this figure are believed to be slip markings, probably on {110}.

Although fracture in embrittled steel is predominantly transgranular, as just shown, an occasional facet is found such as that in Fig. 1c. There the completely altered texture resembles nothing so far found in specimens free from embrittlement. The study of a number of these patterns is convincing that they represent surfaces of individual grains, and that a superficial phase forming along the grain boundaries is directly associated with 475° embrittlement. While at first it seems strange that a grain boundary phase should promote transgranular elasticity, exactly that relationship generally has been agreed upon by previous investigators.

No steps have been taken for direct analysis of this superficial coating; but its general appearance carries a strong similarity with an intergranular coating in cast molybdenum known to be molybdenum oxide.<sup>3</sup> A possibility then presents itself to hypothesize that the phenomenon of 475° embrittlement involves a *chromium oxide*, rather than an intermetallic combination of Fe and Cr.

Further, it is proposed that some attention be paid the protoxide CrO as a possible factor: Chromium monoxide has been identified in several research fields as a prominent constituent of chromiferous steels,<sup>4</sup> and one which deserves further attention by metallurgists. The protoxide is particularly significant because it represents the oxide phase having a direct relationship with oxygen dissolved in the metal—such as FeO in the Fe-O system. Thus it can precipitate and redissolve in crossing its saturation boundary, much in conformity with known effects of thermal treatments on 475° embrittlement.

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## Structure of Spherulites in Nodular Cast Iron

by H. E. Stauss, F. W. Von Batchelder, and E. I. Salkovitz

**E**XISTING information regarding the structure of a spherulite in nodular cast iron is based on optical studies. According to these data, a nodule consists of an aggregate of graphite crystallites radiating from the center, with the closely packed basal planes at right angles to the radii. The  $c$  axes lie along the radii. This view faces some uncertainty in the fact that the  $c$  axis does not represent the accepted direction of fastest growth in graphite.

To supplement the optical information, X-ray studies have now been made. The principle used was to screen the nodule in greater part from the X-ray beam and expose only a minor cap. As successively larger portions of the nodule were introduced into the X-ray beam, any differences in the X-ray patterns could be observed. Such photographs have been taken with chromium radiation and a Laue camera. The graphite nodule itself, about 0.010 to 0.025 in. in diam, was mounted with vaseline on a micrometer screw for control of the linear motion. The nodule rotated about  $45^\circ$  each time that it was translated linearly. The nodules were obtained from magnesium-treated hypereutectic iron by electrolytic solution of the iron in hydrochloric acid.

In Fig. 1a is shown the pattern of the thinnest cap examined. In Fig. 1b is shown the pattern of the same nodule moved 0.003 in. farther into the X-ray beam, and rotated  $45^\circ$  at the same time. Figs. 1a and 1b indicate incomplete circles for graphite (the two outer circles arise from graphite) with the side arcs much weaker than the top and bottom ones. The arcs obtained are themselves not continuous in intensity but vary with maxima of intensity some  $15^\circ$  and  $30^\circ$  apart.

The structure of the nodule that would give rise to such a pattern can be explained as follows. Basically the nodule consisted of small crystallites. The discontinuous character of the diffraction rings demonstrates that the nodule was not composed of randomly oriented crystallites. The strong vertical reflections and the weak lateral reflections show that the reflecting planes were roughly normal to the radii. The absence of sharp reflection spots suggests that the nodule did not contain large crystals. The sharpness of the diffraction rings in their radial direction shows that the variations in intensity along the arcs were not the result of line broadening resulting from extremely small crystals. In the diffraction patterns two rings corresponding to graphite were found. The third and inner ring in the figures originated in the vaseline. The graphite rings correspond to the  $\alpha$  and  $\beta$  lines reflected from the basal planes, showing that the radii of the

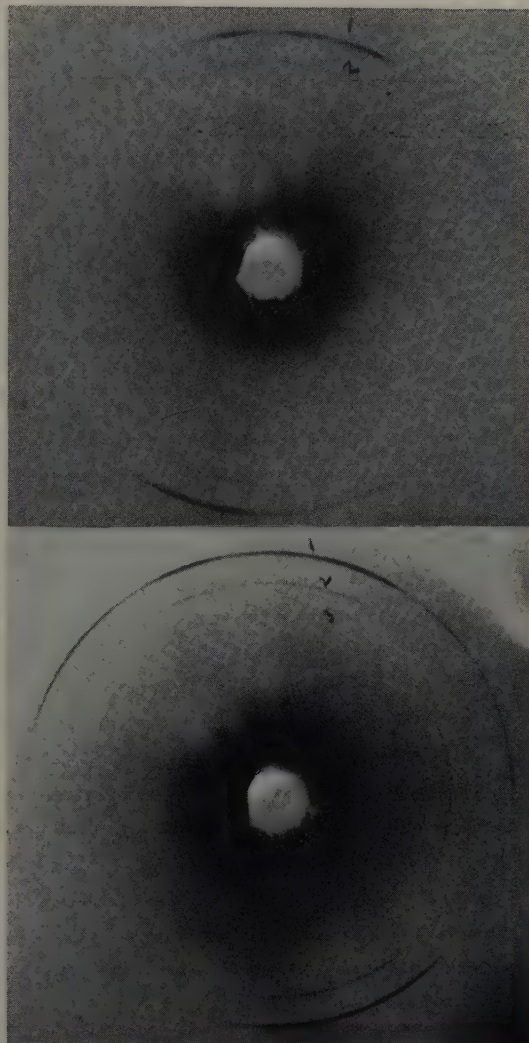


Fig. 1a (top)—Laue pattern of thinnest cap of graphite spherulite from magnesium inoculated hypereutectic iron.

Fig. 1b (bottom)—Laue pattern of spherulite moved 0.003 in. farther into X-ray beam.

nodules are the  $[0001]$  direction normal to the basal planes of graphite.

The picture of the structure that is formed is, therefore, one of aggregates of crystallites. Within each aggregate the  $c$  axes of the crystallites tend to align themselves in the radial direction of the nodule, although these axes deviate somewhat in direction by a continuous variation of angle. Correspondingly the basal planes of the graphite crystallites are generally normal to the radii.

It is a pleasure to acknowledge the assistance of M. C. Bloom and R. P. Dunphy of this laboratory.

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# Deformation and Recrystallization Texture Of Cold-Drawn OFHC Copper Wire

by W. A. Backofen

THE texture of cold-drawn copper wire has been described most often as a composite of  $[111]$  and  $[100]$  directions aligned parallel to the wire axis.<sup>1</sup> Hibbard<sup>2</sup> suggested that sufficient reduction will result in a single  $[111]$  texture and reported that after a reduction in area of 96.4 pct, such a texture was nearly obtained. Other work<sup>3, 4</sup> has shown that recrystallization within the temperature range of 300° to 1000°C does not alter the texture established by cold-drawing. In general, however,

directions aligned parallel to the wire axis. Supplementary measurements with a Geiger-Mueller counter of the intensity of reflection from  $(111)$  planes showed that the  $[111]$  component was much more predominant than the  $[100]$ .

Additional specimens of the drawn and etched wire were annealed in a salt bath at temperatures from 300° to 450°C. The texture of the recrystallized wire was studied with the same technique applied to the cold-drawn wire. Fig. 1b is an X-ray

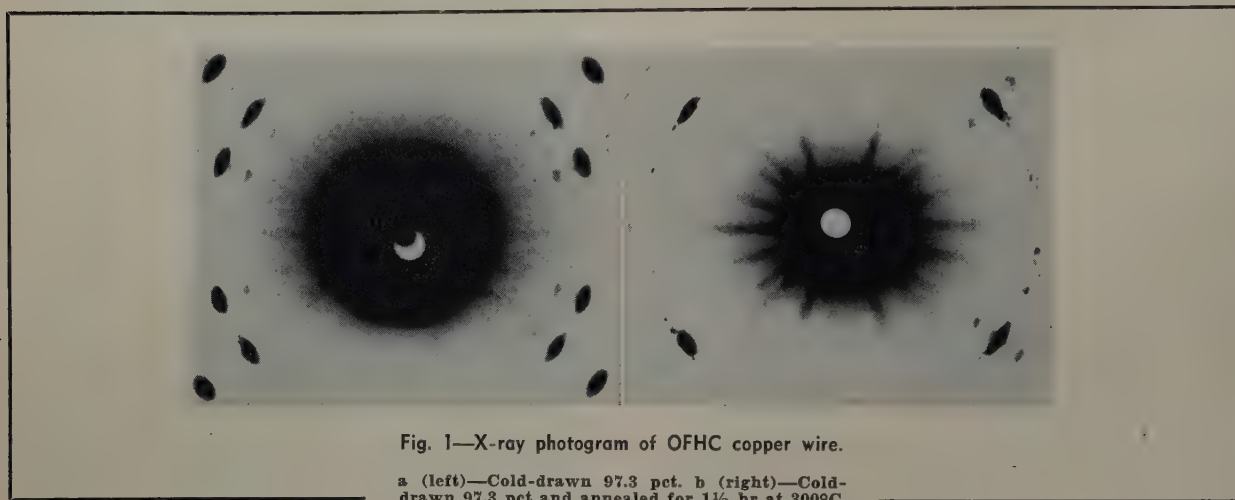


Fig. 1—X-ray photograph of OFHC copper wire.

a (left)—Cold-drawn 97.3 pct. b (right)—Cold-drawn 97.3 pct and annealed for 1½ hr at 300°C.

The wire axis is in the vertical position. The inner diffraction ring is from  $\{111\}$  planes. The outer diffraction ring is from  $\{200\}$  planes.

the texture of cold-drawn and annealed copper wire is not as well defined as the deformation texture. In the work reported here it was found that the double-fiber, deformation texture persists even after a reduction in area of 97.3 pct, and after recrystallization the texture is practically all  $[100]$ .

The wire used in this work was prepared in the following way. A ¾-in. diam length of annealed OFHC copper was cold-drawn to a diameter of ⅛ in., a reduction in area of 97.3 pct. Each step in the drawing operation brought about a reduction in area that varied from 6 to 10 pct. Short lengths of this wire were etched in a 50-pct solution of nitric acid to a diameter of approximately 0.01 in.

The texture of the cold-drawn specimens was determined with the conventional X-ray transmission diffraction technique using filtered copper radiation. The X-ray beam was directed perpendicularly to the wire axis and the diffraction rings were recorded on a flat film. Fig. 1a is typical of the photographs obtained and reveals that the cold-drawing schedule described above introduces a distinct, double-fiber texture with both  $[111]$  and  $[100]$

photogram of a specimen annealed for 1½ hr at 300°C and is typical of those obtained from recrystallized specimens. The photogram shows that recrystallization of this material is accompanied by the almost complete elimination of the  $[111]$  component of the deformation texture. A pronounced strengthening of the  $[100]$  component was evident from intensity measurements with a Geiger-Mueller counter.

In summary, the deformation texture of cold-drawn OFHC copper wire, after a reduction in area of 97.3 pct, may still be described as a composite of  $[111]$  and  $[100]$  directions aligned parallel to the wire axis. Recrystallization of such wire at temperatures from 300° to 450°C introduces a texture which consists almost entirely of a  $[100]$  alignment.

## Acknowledgment

Sidney Rolle of the Scomet Engineering Co. generously supplied the OFHC copper used in this work.

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TN 53E. Manuscript, Dec. 4, 1950.



# Intergranular Energy of Iron and Some Iron Alloys

by Lawrence H. Van Vlack

The energy of the  $\gamma$ -iron grain boundary was determined to be 850 ergs per  $\text{cm}^2$  at  $1105^\circ\text{C}$ . The  $\alpha/\alpha$  and the  $\alpha/\gamma$  boundaries possess somewhat less energy. The microstructures of several iron alloys are discussed in terms of the interfacial energy relationships.

THE dependence of the shape of liquid interfaces upon their energies has been studied for some time.<sup>1-3</sup> Recently, Smith<sup>4</sup> concluded that many of the microstructures observed in metals may be attributed to the energies of the interfaces between the grains and phases.

While the energies of liquid surfaces have been measured by numerous different methods,<sup>5</sup> only two attempts have been made to determine experimentally the energy of surfaces involving crystalline solids. Udin, Shaler, and Wulff<sup>6</sup> used a procedure introduced by Berggren<sup>7</sup> to measure the surface tension of solid copper. It consisted of determining the load required on a thin copper wire so that the surface tension was counteracted, and no net strain resulted. Bailey and Watkins<sup>8</sup> used a different technique and were able to determine both the surface tension of copper and the tension of the copper grain boundary. They measured the contact angle which liquid lead makes against a copper surface. They then calculated the above energies from the surface energy of liquid lead by using the Pb vs. Cu/Cu\* dihedral angle and the surface groove angle formed during thermal etching. They obtained a value of 1800 dynes per cm for the surface tension of clean copper and approximately 640 dynes per cm for the tension of copper grain boundaries. The former value was somewhat higher than Udin's value of 1500 dynes per cm.

This paper includes a determination of the energy of the  $\gamma$ -iron grain boundary. In addition, the microstructural relationships of several other metallic and nonmetallic phases with iron were examined and an attempt was made to interpret the observed structures in terms of interfacial energy relationships.

## Theoretical Considerations

In a three-phase material containing a solid and two liquids, there may be two solid/liquid interfaces, one liquid/liquid interface and one inter-

granular interface. Liquid/liquid interfacial energies can be measured directly. Therefore, by determining the energy of such an interface and by measuring the required interfacial angles,<sup>9</sup> the energies of the interfaces involving solids may be obtained.<sup>10</sup> They may be shown schematically as in Fig. 1.

The above procedure requires the following assumptions: 1—The interfacial energies are, in general, unaffected by boundary orientation, and 2—the shapes of the interfaces are unaltered between annealing and sectioning for microscopic examination. The first assumption is good to a first approximation as shown by Dunn and Lionetti<sup>11</sup> except for a few critically orientated boundaries. Two conditions may alter the shape of a boundary upon cooling: 1—Precipitation of dissolved material upon one side of the interface, and 2—a change in volume during the transition from one phase modification to another. The former must be detected by microscopic observation. The latter may become appreciable in systems containing an interface between two liquids which solidify after annealing. However, possible movement of the two-liquid interface may be checked in the system diagrammed in Fig. 1 by measuring  $\theta$ , for example, and comparing it with its value as calculated from the other interfacial angles by:

$$\tan \theta_2 = \frac{-\sin \theta_3}{\cos \frac{\theta_5}{2}} + \cos \theta_2 \quad [1]$$
$$\cos \frac{\theta_4}{2}$$

The choice of a suitable pair of liquids is limited by several factors. The relative values of the several

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This paper represents part of a thesis by the author submitted in partial fulfillment of requirements of the degree of Doctor of Philosophy to the University of Chicago.

\* This notation, first employed by Smith<sup>4</sup> and followed by others, indicates the angle formed by one phase between the two adjacent grains (or phases).

interfacial energies should be such that the interfacial angles— $\theta_s$ ,  $\theta_1$ , and  $\theta_2$ —are as small as possible but still are greater than zero. The interface should be mobile enough so that it adjusts to the equilibrium shape in a reasonably short length of time. In addition, neither liquid should react with the solid to give a fourth phase.

Few liquid pairs contain all the above features. The two liquids, "copper" and "copper sulphide," most nearly met the requirements for use with iron. As such, they were not pure liquids, as shown in Fig. 2. Likewise, the iron surface became saturated with copper and sulphur.

The interfacial energy,  $\gamma$ , between liquid "copper" and liquid "copper sulphide" was measured by the differential capillary depression of their interface in two fused-silica tubes of unequal radii, as diagrammed in Fig. 3, in which:

$$\gamma = \frac{\Delta H g (D-d)}{2 \cos \phi} \frac{(b_1 b_2)}{b_2 - b_1} \tag{2}$$

The contact angle,  $\phi$ , with these phases was  $180^\circ$  (or  $0^\circ$  as the case may be). The difference in meniscus levels,  $\Delta H$ , was determined radiographically;  $D$  and  $d$  are the densities of the two liquids;  $g$  is  $980.6 \text{ cm per sec}^2$ ; and  $b_1$  and  $b_2$  were the radii of curvatures for the centers of the two menisci.

The radii of curvatures were not identical with the tube radii because the capillaries and the density differentials were too large for the menisci to approximate a hemisphere. However, the shape of a meniscus surface with a contact angle of  $180^\circ$  is the same as the surface of a drop with a contact angle of  $90^\circ$ , as shown in Fig. 4. Therefore, the radii of surface curvature may be calculated from the tube radii and the approximate capillary constant by following Sugden's<sup>13</sup> treatment of Bashforth and Adams' tables.

### Experimental Technique

The procedure chosen for the determination of the intergranular energy of iron required two separate experiments: 1—A determination of the relative energies of the several interfaces in an iron-copper-copper sulphide alloy, and 2—a determination of the energy of the liquid copper/liquid copper sulphide interface.

The former was obtained from the dihedral angles in a sample containing the three phases. The angles were measured with a protractor on a rotating micrometer ocular at a magnification of about X600. At least 100, and as many as 200, angles were measured between each of the required interfaces. Following Harker and Parker's work<sup>9</sup> the most

frequently observed angles were considered to be within  $\pm 5^\circ$  of the true interfacial angle.

The samples for microscopic examination were made by inserting iron and copper filings and sulphur powder into an iron crucible which was made by drilling a 3/32 in. hole into a 3/16 in. iron rod. These were compressed with a tapered iron plug. The latter also served to retain, first the sulphur, and then later the liquid in the compact during the annealing. The iron used was Puron which contained 0.17 pct O by vacuum fusion analysis and about 0.1 pct other elements. The copper contained 0.008 pct Fe and smaller traces of Ni, Si, and Ag. The copper sulphide was made both by subjecting the above copper to sulphur vapors in an evacuated sealed tube at  $500^\circ\text{C}$  and by mixing copper and sulphur in the compacts.

Fig. 5 gives the diagrammatic layout of the furnace equipment. The specimens were annealed under a hydrogen atmosphere and quenched into a water stream. Temperatures were measured with chromel-alumel thermocouples within the radiation muffles.

The capillary depression of the two-liquid interface was obtained under a nitrogen atmosphere after initial evacuation. After the copper and copper sulphide had melted, the two capillaries, 1 in. long, were pushed through the two-liquid interface by an iron weight. This iron weight and iron in the bottom of the crucible also served to saturate the liquids with iron. The crucible tube was placed in the furnace in a position so that a minimum amount of "copper" or "copper sulphide" masked the menisci. The liquids were allowed to stand at least 30 min before the X-ray exposure, during which time the crucible was vibrated at intervals so that better assurance of correct meniscus differentials was obtained.

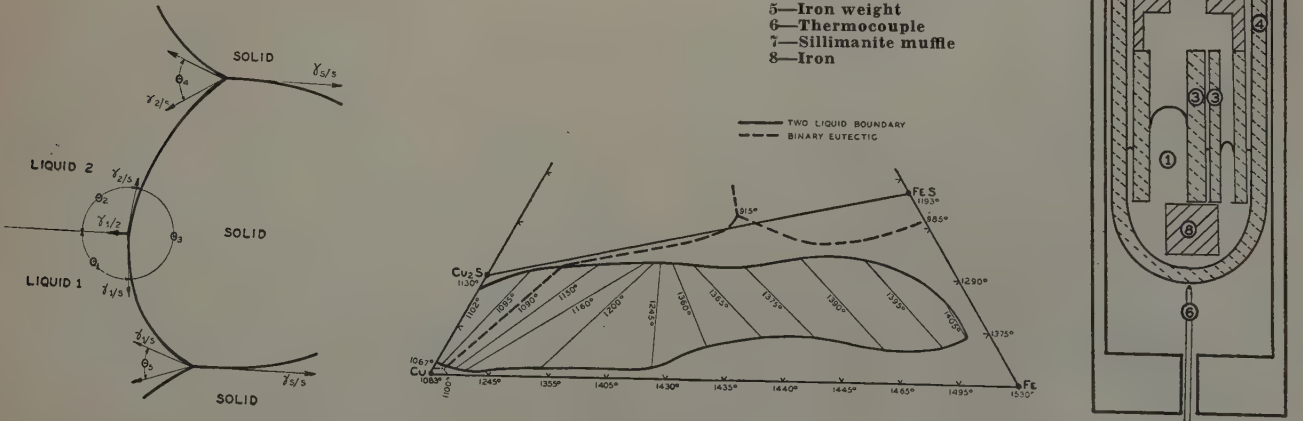
The liquid densities were measured by determining the maximum pressures required to bubble nitrogen through different depths of the liquids, as shown in Fig. 6.

Fig. 1 (left)—Schematic representation of the interfacial energy relationships in a three-phase alloy.

$$\gamma_{S/S} = \frac{\theta_5 \sin \theta_2}{2 \sin \theta_3} \gamma_{1/2}$$

Fig. 2 (center)—Fe-Cu-Cu<sub>2</sub>S-FeS system.<sup>12</sup>

Fig. 3 (right)—Capillary tube arrangement for the determination of the energy of the liquid Cu/liquid Cu<sub>2</sub>S interface.





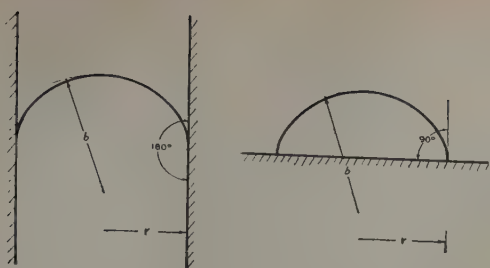


Fig. 4—*a* (left)—Meniscus surface with 180° contact angle. *b* (right)—Drop surface with 90° contact angle.

Contact radius,  $r$ . Radius of surface curvature,  $b$ .

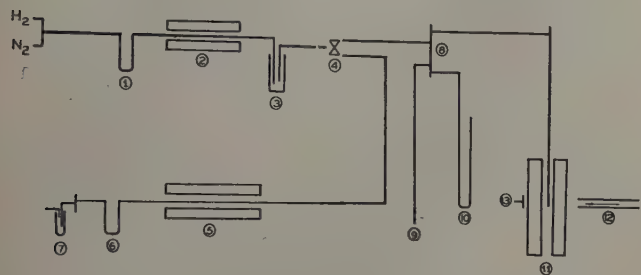


Fig. 5—Diagrammatic layout of laboratory equipment.

- |                              |                            |
|------------------------------|----------------------------|
| 1—Drying tube                | 8—Manifold                 |
| 2—Deoxidation furnace        | 9—Vacuum pump (mechanical) |
| 3—Liquid N <sub>2</sub> trap | 10—Hg manometer            |
| 4—Two-way stopcock           | 11—X-ray furnace           |
| 5—Annealing furnace          | 12—220 kv X-rays           |
| 6—Drying tube                | 13—Film holder             |
| 7—Trap and bubbler           |                            |

The radii of the capillaries were used to calculate the radii of curvature of the two-liquid interface at the crown of the menisci. The former were measured as two perpendicular diameters at each end of the 1-in. capillary tube.

### Energy of the Two-Liquid Interface

The density determinations required for the calculation of the interfacial energies are presented in Table I. The energies of the interface between liquid copper and liquid copper sulphide at several temperatures are given in Table II. The energies were determined for both iron-saturated and iron-free liquids.

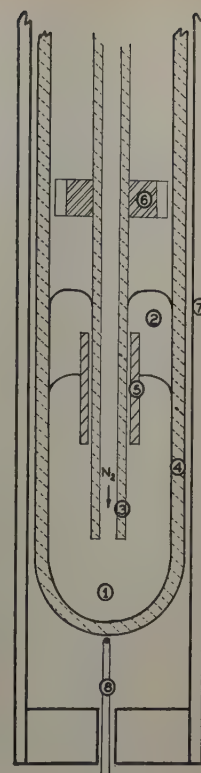
The energy of the interface decreased with increasing temperature over the temperature range examined, as shown in Fig. 7. This decrease would continue to zero near the critical temperature where the two liquids become mutually miscible.<sup>5</sup> Reuleaux<sup>12</sup> showed that this critical temperature is slightly above 1400°C when the two liquids in the Cu-Fe-S system are saturated with iron, as indi-

Table I. Density Determinations

| Test | Liquid          | Saturated With   | Temperature, °C | Density, G per Cm <sup>3</sup> |
|------|-----------------|------------------|-----------------|--------------------------------|
| 202  | Copper          | Sulphur          | 1115            | 7.8 <sub>2</sub>               |
|      | Copper          | Sulphur          | 1158            | 7.7 <sub>8</sub>               |
|      | Copper          | Sulphur          | 1208            | 7.7 <sub>1</sub>               |
| 204  | Copper sulphide | Copper           | 1125            | 5.3 <sub>7</sub>               |
|      | Copper sulphide | Copper           | 1126            | 5.4 <sub>2</sub>               |
|      | Copper sulphide | Copper           | 1158            | 5.3 <sub>7</sub>               |
|      | Copper sulphide | Copper           | 1207            | 5.3 <sub>8</sub>               |
| 203  | Copper          | Iron and sulphur | 1125            | 8.0 <sub>6</sub>               |
|      | Copper          | Iron and sulphur | 1125            | 8.1 <sub>1</sub>               |
|      | Copper          | Iron and sulphur | 1154            | 8.0 <sub>1</sub>               |
|      | Copper          | Iron and sulphur | 1209            | 7.9 <sub>8</sub>               |
| 205  | Copper sulphide | Iron and copper  | 1154            | 5.0 <sub>5</sub>               |
|      | Copper sulphide | Iron and copper  | 1153            | 5.1 <sub>2</sub>               |
|      | Copper sulphide | Iron and copper  | 1206            | 5.0 <sub>6</sub>               |
|      | Copper sulphide | Iron and copper  | 1119            | 5.1 <sub>3</sub>               |

Fig. 6—Sketch of crucible for the determination of liquid densities.

- 1—Liquid Cu
- 2—Liquid Cu<sub>2</sub>S
- 3—Fused silica tube
- 4—Fused silica crucible
- 5—Iron sleeve
- 6—Carbon centering block
- 7—Sillimanite muffle
- 8—Thermocouple



cated in Fig. 2. An extrapolation of the interfacial energies between the iron-saturated liquids to zero at the critical temperatures is in accordance with the above expectations. The interfacial energy of the iron-free liquids decreased less with increased temperatures than did the energy between the iron-saturated liquids.

### Intergranular Energy of $\gamma$ Iron

The observed dihedral angles, from which the relative energies of the interfaces in the three-phase Fe-Cu-Cu<sub>2</sub>S alloy were determined, are shown in Fig. 8 as frequency distribution plots. In addition to the plots for the five angles to the nearest 10°, Fig. 8A to 8E, the dihedral angles observed for Fe vs. Cu/Cu<sub>2</sub>S were plotted to the nearest 2°. While the resulting accuracy was not increased propor-

Table II. Liquid Copper-Liquid Copper Sulphide Interfacial Energy Determinations

| Test                | Temperature, °C | $R$ , Cm | $r$ , Cm | $\Delta H$ ,* Cm  | $\alpha$ , <sup>2</sup> Cm <sup>2</sup> | $\alpha^2$ (Corrected), <sup>†</sup> Cm <sup>2</sup> | $\gamma$ Ergs per Cm <sup>2</sup> |
|---------------------|-----------------|----------|----------|-------------------|-----------------------------------------|------------------------------------------------------|-----------------------------------|
| Saturated With Iron |                 |          |          |                   |                                         |                                                      |                                   |
| 207E                | 1162            | 0.323    | 0.092    | 0.51 <sub>4</sub> | 0.066 <sub>1</sub>                      | 0.60 <sub>9</sub>                                    | 86                                |
| 207F                | 1124            | 0.323    | 0.092    | 0.57              | 0.073 <sub>6</sub>                      | 0.68 <sub>0</sub>                                    | 98                                |
| 207G                | 1129            | 0.323    | 0.092    | 0.57              | 0.072 <sub>6</sub>                      | 0.68 <sub>0</sub>                                    | 98                                |
| 207H                | 1208            | 0.323    | 0.092    | 0.42 <sub>7</sub> | 0.054 <sub>0</sub>                      | 0.50 <sub>2</sub>                                    | 71                                |
| 207J                | 1209            | 0.323    | 0.092    | 0.42 <sub>7</sub> | 0.054 <sub>0</sub>                      | 0.50 <sub>2</sub>                                    | 71                                |
| 206A                | 1154            | 0.333    | 0.092    | 0.52 <sub>3</sub> | 0.066 <sub>0</sub>                      | 0.61 <sub>5</sub>                                    | 87.5                              |
| 206B                | 1154            | 0.333    | 0.092    | 0.54 <sub>3</sub> | 0.069                                   | 0.63 <sub>5</sub>                                    | 90                                |
| 186B                | 1153            | 0.156    | 0.112    | 0.16 <sub>8</sub> | 0.064 <sub>0</sub>                      | 0.060 <sub>3</sub>                                   | 86                                |
| 212A                | 1134            | 0.167    | 0.106    | 0.24 <sub>2</sub> | 0.070 <sub>2</sub>                      | 0.065 <sub>6</sub>                                   | 95                                |
| 212B                | 1124            | 0.167    | 0.106    | 0.23 <sub>2</sub> | 0.067 <sub>6</sub>                      | 0.062 <sub>7</sub>                                   | 91                                |
| 212C                | 1186            | 0.167    | 0.106    | 0.20 <sub>4</sub> | 0.059                                   | 0.054                                                | 77                                |
| Iron Free           |                 |          |          |                   |                                         |                                                      |                                   |
| 210A                | 1131            | 0.230    | 0.112    | 0.38              | 0.082 <sub>5</sub>                      | 0.076 <sub>3</sub>                                   | 90                                |
| 210C                | 1131            | 0.230    | 0.112    | 0.38              | 0.082 <sub>5</sub>                      | 0.076 <sub>3</sub>                                   | 90                                |
| 210D                | 1159            | 0.230    | 0.112    | 0.36 <sub>4</sub> | 0.079 <sub>5</sub>                      | 0.073 <sub>7</sub>                                   | 87                                |
| 210E                | 1216            | 0.230    | 0.112    | 0.33              | 0.072 <sub>3</sub>                      | 0.066 <sub>4</sub>                                   | 76.5                              |

\* Corrected for the divergence of X-rays.

<sup>†</sup> Corrected for meniscus shapes.

Table III. Dihedral Angles in the Fe-Cu-Cu<sub>2</sub>S Alloy at 1105°C

| Dihedral Angle              | Observed | Calculated from Eq 1 |
|-----------------------------|----------|----------------------|
| Cu vs. Fe/Cu <sub>2</sub> S | 95°      | 77°                  |
| Cu <sub>2</sub> S vs. Fe/Cu | 100°     | 115°                 |
| Fe vs. Cu/Cu <sub>2</sub> S | 168°     |                      |
| Cu <sub>2</sub> S vs. Fe/Fe | 50°      |                      |
| Cu <sub>2</sub> S vs. Fe/Fe | 25°      |                      |

Table IV. Interfacial Energies of the Fe-Cu-Cu<sub>2</sub>S Alloy at 1105°C

| Interface                             | Energy, Ergs per Cm <sup>2</sup> |
|---------------------------------------|----------------------------------|
| Liquid copper/liquid copper sulphide  | 100                              |
| Liquid copper/ $\gamma$ iron          | 430                              |
| Liquid copper sulphide/ $\gamma$ iron | 470                              |
| $\gamma$ iron/ $\gamma$ iron          | 850                              |

tionally in the latter case, the smaller overall variation in observed angles did permit a closer estimation of the true dihedral angle. This was desirable because it is a large angle and its sine function is used in the calculation of the relative interfacial energies.

There is evidence that the two-liquid interface moved on solidification. On the basis of the relative interfacial energies of the two iron-liquid interfaces as determined from the dihedral angles of the two liquids between iron grains, the Cu<sub>2</sub>S vs. Fe/Cu dihedral angle decreased about 15°, as given in Table III. The Cu vs. Fe/Cu<sub>2</sub>S angle increased by a similar amount. This movement may be associated with the lower specific volume of the solid, since the interface moved toward the copper sulphide which solidified first. It would not be expected that all of the two-liquid interfaces would be moved to give identical solid interfacial angles. The breadth of the frequency distribution curves, shown in Fig. 8C and 8D, supports this expectation.

Inasmuch as there was an apparent movement of the two-liquid interface during solidification, the relative and calculated dihedral energies were determined on the basis of the angles between interfaces involving a solid. These energies for the alloy of  $\gamma$  iron, liquid copper, and liquid copper sulphide at 1105°C are given in Table IV. It may be pointed

Table V. Dihedral Angles of Cu-Fe Alloys

| Test | Temperature, °C | Dihedral Angle             | Observed |
|------|-----------------|----------------------------|----------|
| 281  | 1000            | Cu vs. $\gamma/\gamma$     | 70°      |
| 281  | 1000            | $\gamma$ vs. Cu/Cu         | 110°     |
| 299  | 825             | Cu vs. $\alpha/\alpha$     | 95°      |
| 299  | 825             | $\alpha$ vs. Cu/Cu         | 110°     |
| 237  | 1160            | Liquid vs. $\gamma/\gamma$ | 30°      |
| 238  | 1220            | Liquid vs. $\gamma/\gamma$ | 30°      |

Table VI. Interfacial Energies of Cu-Fe Alloys

| Temperature, °C | Interface          | Relative Energy*  |
|-----------------|--------------------|-------------------|
| 1000            | $\gamma/\gamma$    | 1.00              |
| 1000            | $\gamma/\text{Cu}$ | 0.61              |
| 1000            | Cu/Cu              | 0.70              |
| 825             | Cu/Cu              | 0.7               |
| 825             | $\alpha/\text{Cu}$ | 0.6               |
| 825             | $\alpha/\alpha$    | 0.85              |
| 1160            | Liquid/ $\gamma$   | 0.51 <sub>7</sub> |
| 1220            | Liquid/ $\gamma$   | 0.51 <sub>7</sub> |

\* Reference value.

out, however, that since the interfacial angles involving the two-liquid interface were near 90°, and their sine function was concerned, errors corrected by this precaution were relatively small. For example, the energy of the liquid copper/ $\gamma$ -iron interface would have been 470 ergs per cm<sup>2</sup> instead of 430 ergs per cm<sup>2</sup>.

An effort was made to determine the intergranular energy of iron at higher temperatures. However, at temperatures much above 1090°C, where the two liquids form, iron precipitated from the liquid copper sulphide onto the iron interface during quenching to obliterate partially the original iron/copper sulphide interface. This happened even with the most severe quench. Consequently, the relative interfacial energies were not estimated for the higher temperatures.

The accuracies of the calculated interfacial energies in Table IV are limited chiefly by the accuracy in the measurement of the Fe vs. Cu/Cu<sub>2</sub>S dihedral angle. A 15 pct possible error exists with a 2° error in that angle. An approximate check on the above value of 850 ergs per cm<sup>2</sup> for the intergranular energy of  $\gamma$  iron at 1105°C may be obtained from Bailey and Watkins<sup>8</sup> determination of the copper grain boundary energy. From the dihedral angle measurements, the relative energies of the iron and copper grain boundaries in iron-copper alloys at

Table VII. Relative Interfacial Energies of  $\alpha$ - $\gamma$  Sulphide Alloy

| Interface                      | Course of Calculation* | Relative Value† |
|--------------------------------|------------------------|-----------------|
| $\gamma$ iron/ $\gamma$ iron   | 1, 3, 2                | 1.0             |
|                                | 1, 3, 4, 5, 2          | 1.02            |
|                                | 2, 3, 1                | 0.98            |
|                                | 2, 5, 4, 3, 1          | 0.99            |
|                                | Avg                    | 1.00            |
| $\gamma$ iron/ $\alpha$ iron   | 2                      | 0.71            |
|                                | 2, 5, 4, 3             | 0.74            |
|                                | 1, 3                   | 0.72            |
|                                | 1, 3, 4, 5             | 0.69            |
|                                | Avg                    | 0.72            |
| $\alpha$ iron/ $\alpha$ iron   | 1, 3, 4                | 0.89            |
|                                | 2, 5                   | 0.91            |
|                                | 1, 3, 5                | 0.92            |
|                                | 2, 3, 4                | 0.86            |
|                                | Avg                    | 0.90            |
| Sulphide liquid/ $\gamma$ iron | 1                      | 0.65            |
|                                | 2, 3                   | 0.64            |
|                                | 2, 5, 4, 3             | 0.67            |
|                                | Avg                    | 0.65            |
| Sulphide liquid/ $\alpha$ iron | 1, 3                   | 0.69            |
|                                | 1, 3, 5, 4             | 0.72            |
|                                | 2, 5, 4                | 0.71            |
|                                | 2, 3                   | 0.67            |
|                                | Avg                    | 0.70            |

\* See Fig. 9.

† Reference value.

Table VIII. Relative Interfacial Energies of Liquid Sulphide/Iron Interfaces

| Test | Temperature, °C | Dihedral Angle Liquid vs. Fe/Fe | Liquid-Iron Interfacial Energy Fe/Fe = 1.0 | Fe Content of Liquid, <sup>17</sup> Pct |
|------|-----------------|---------------------------------|--------------------------------------------|-----------------------------------------|
| 260  | 1026            | 30°                             | 0.51 <sub>8</sub>                          | 70                                      |
| 256  | 1198            | 25°                             | 0.51 <sub>2</sub>                          | 74                                      |
| 258  | 1301            | 0                               | $\leq 0.50$                                | 78                                      |
| 277  | 1325            | 0                               | $\leq 0.50$                                | 80                                      |



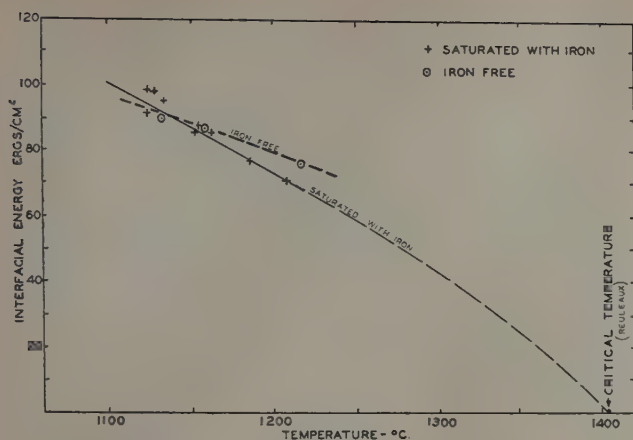


Fig. 7—Energy of the liquid Cu/liquid  $\text{Cu}_2\text{S}$  interface.

1000°C are 1.0 and 0.7 respectively, Tables V and VI. Therefore, using their approximate value of 640 ergs per  $\text{cm}^2$  for the energy of the copper grain boundary, the intergranular energy of copper-saturated iron would be 915 ergs per  $\text{cm}^2$ .

### Relative Intergranular Energies of $\alpha$ and $\gamma$ Iron

The above measurements for the intergranular energy of iron were made on copper-saturated  $\gamma$  iron. Alpha iron cannot be in equilibrium with the

copper-saturated  $\gamma$  iron,<sup>14</sup> and a liquid pair was not found which was suitable for use in the temperature range of  $\alpha$  iron without the addition of ferrite-forming alloying elements. However, if it may be assumed that the energy of the copper grain boundary is somewhat constant with lowering temperatures, the relative intergranular energy of  $\alpha$  and  $\gamma$  iron may be determined by annealing copper-iron alloys below their eutectoid temperature. This gives a value for the  $\alpha$ -iron grain boundary as 0.85 that of the  $\gamma$ -iron boundary, as shown in Tables V and VI.

A more direct comparison of the energy of the  $\alpha$  and  $\gamma$ -iron grain boundaries may be made by measuring the dihedral angles in a duplex,  $\alpha$ - $\gamma$  alloy. This was done by adding 4 pct Si and 0.2 pct C to ingot iron. To give a third phase, 0.26 pct S was added and thus offered a means of checking the relative values.<sup>4</sup> See Fig. 10. Table VII shows these values for the recrystallized alloys at 1150°C. These are calculated from the interfacial angles shown in Fig. 9.

The energy of the  $\alpha/\alpha$  boundary is about 0.9 that of the  $\gamma/\gamma$  boundary. The  $\alpha/\gamma$  boundary energy was less than either the  $\alpha/\alpha$ , or the  $\gamma/\gamma$  boundary energy—about 0.7 of the latter.

The discrepancy appearing in the relative values of the energy of the  $\alpha/\alpha$  boundary as determined by the two methods must be attributed, at least in part,

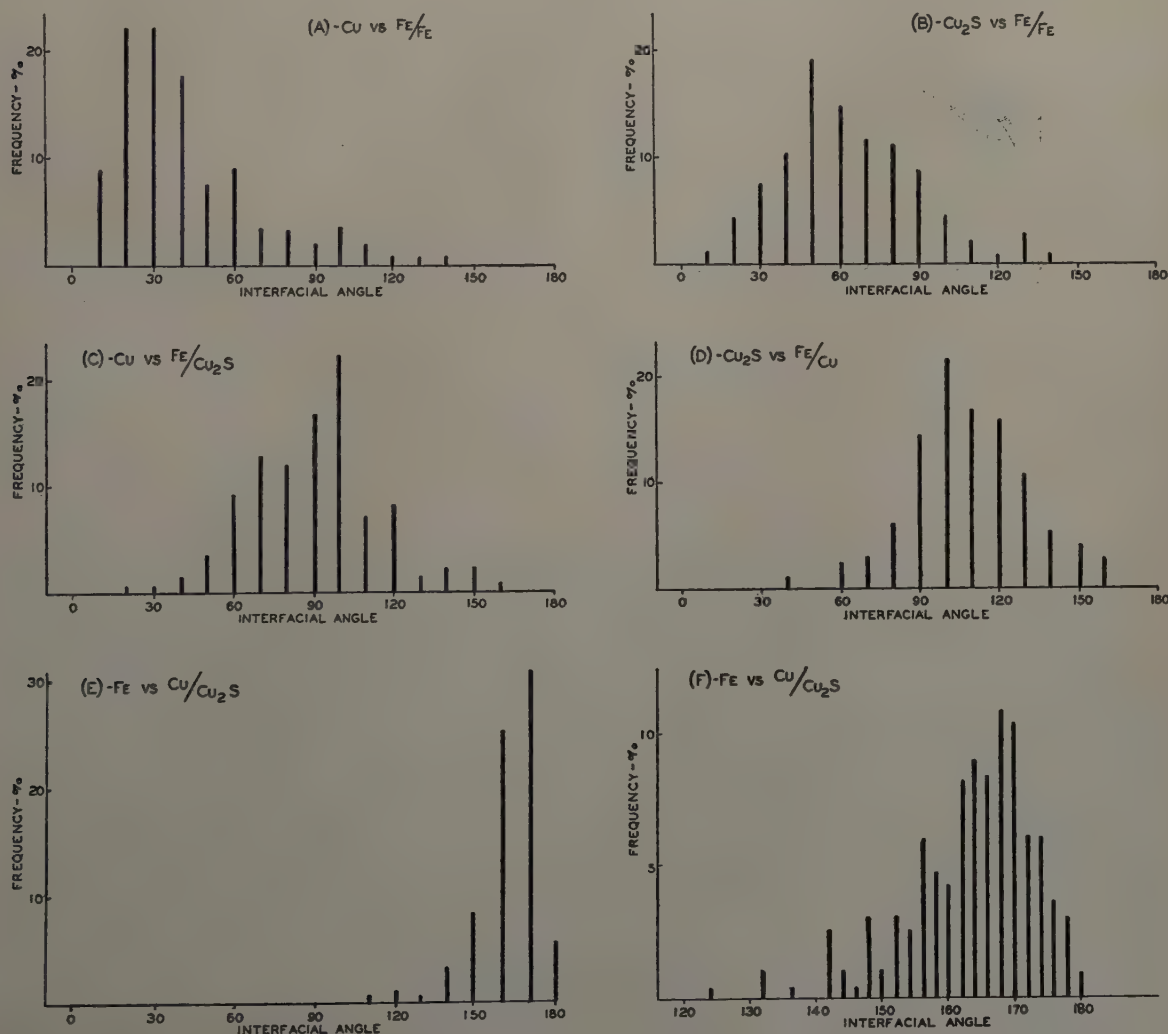


Fig. 8—Test No. 252. Distribution of the observed dihedral angles in the Fe-Cu- $\text{Cu}_2\text{S}$  alloy. Annealed at 1105°C for 1 hr and quenched.

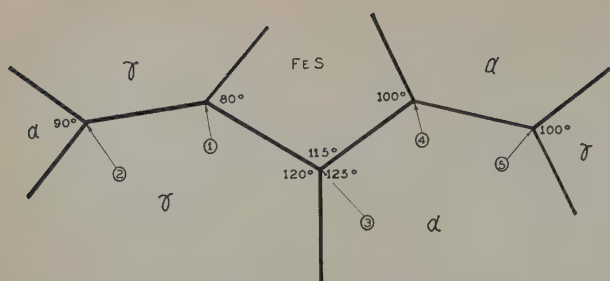


Fig. 9—Schematic representation of interfacial angles in an  $\alpha$ - $\gamma$ -FeS alloy, Fig. 10.

to the differences in compositions of the iron phase in the presence of silicon and copper.

The appearance of the duplex,  $\alpha$ - $\gamma$  alloy, given in Fig. 11, suggests that there is an orientation of the two-phase boundary with lower interfacial energy. On solidification, an alloy of this composition forms chiefly ferrite, but on cooling, austenite forms from part of the ferrite.<sup>15</sup> As indicated in Fig. 11, this proceeds along specific crystal directions. Annealing for extended periods of time does not reduce the interfacial area noticeably. Presumably an increase in energy would be required to move the interface even though a reduction of surface area would be obtained. If the alloy is recrystallized by hot working in the same temperature range, this preferred boundary orientation disappears and a normal two-phase structure is obtained, shown in Fig. 12.

### Relative Energies of Iron/Liquid Interfaces

**Sulphur-Containing Liquids:** The distribution of an iron-sulphur liquid in iron alloys has been of interest to metallurgists. In order to gain some information regarding the effect of interfacial energies upon this distribution, a series of samples, which were quenched from their annealing temperatures, were examined microscopically. The dihedral angles formed between iron grains by liquids containing iron sulphide at several temperatures above the eutectic are given in Table VIII.

The iron used in this case had been remelted under hydrogen to remove essentially all of the oxygen. At 1300°C, the liquid spread between most of the iron grains, as shown in Fig. 13, indicating that the energy of the liquid-iron interface had decreased to one half, or less, of the intergranular energy of iron. Some fewer obvious exceptions are

illustrated by Fig. 13 where the observed dihedral angles were still finite. Presumably a slight variation existed in the boundary energies with orientation, and as such, all of the dihedral angles did not become zero at once.

The decrease of the relative energy of the liquid-iron interface with increasing temperature cannot be assigned to the temperature rise alone.<sup>16</sup> The composition of the liquid changes to higher iron contents along the liquidus of the iron-iron sulphide system.<sup>17</sup> In that situation, there is greater similarity between the composition of the two phases so that atoms at the interface require less additional energy by virtue of their position.

The presence of oxygen in the sulphide-containing liquid showed comparatively little effect on the relative liquid/iron interfacial energy at temperatures below 1200°C, as given in Table IX. However, at 1300°C, the dihedral angle did not drop to zero as it did with the oxygen-free liquid, shown in Fig. 15. The explanation of this difference may lie with the liquidus relationships in the Fe-FeS-FeO system. On the basis of Vogel and Fulling's<sup>18</sup> and Gurry,

Table IX. Relative Interfacial Energies of Liquid Sulphide-Oxide/Iron Interfaces

| Test | Temperature, °C | Dihedral Angle Liquid vs. Fe/Fe | Liquid-Iron Interfacial Energy Fe/Fe = 1.0 | FeS/FeO (Approx.) | Fe Content of Liquid,* Pct |
|------|-----------------|---------------------------------|--------------------------------------------|-------------------|----------------------------|
| 75   | 1000            | 35°                             | 0.52 <sub>5</sub>                          | 10/1              | 69                         |
| 62   | 1150            | 25°                             | 0.51 <sub>2</sub>                          | 10/1              | 71                         |
| 104  | 1215            | 20°                             | 0.50 <sub>7</sub>                          | 10/1              | 73                         |
| 150  | 1300            | 15°                             | 0.50 <sub>4</sub>                          | 10/1              | 75                         |
| 276  | 1325            | 25°                             | 0.51 <sub>2</sub>                          | 8/2               | 73                         |

\* Fig. 14.

Darken and Anderson's<sup>19</sup> work, the liquidus isotherms for this system are shown in Fig. 14. The oxygen-free liquid is richer in iron than the oxygen-containing liquid at 1300°C. This difference is not so marked at 1200°C or lower.

A phase consisting of equimolecular amounts of FeS and FeTe may be liquid in the presence of  $\alpha$  iron. Thus, a general comparison of the relative interfacial energies, liquid/solid and solid/solid may be made when the solid is either  $\alpha$  or  $\gamma$  iron. In both

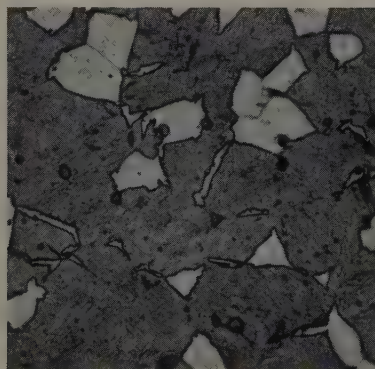


Fig. 10—Test No. 295. Three-phase iron-silicon-carbon-sulphur steel.

4.10 pct Si, 0.22 pct C, 0.26 pct S. Hand forged at 1050°C to 50 pct reduction. Annealed at 1150°C for 30 min and quenched. Nital etch. X500. Area reduced approximately 33 pct for reproduction.

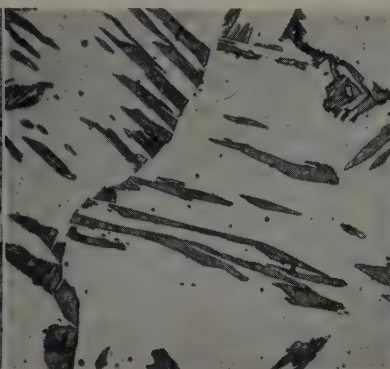


Fig. 11—Test No. 283.  $\alpha$ - $\gamma$  steel.

3.82 pct Si, 0.16 pct C. Annealed at 1005°C for 48 hr and quenched. Nital etch. X500. Area reduced approximately 33 pct for reproduction.

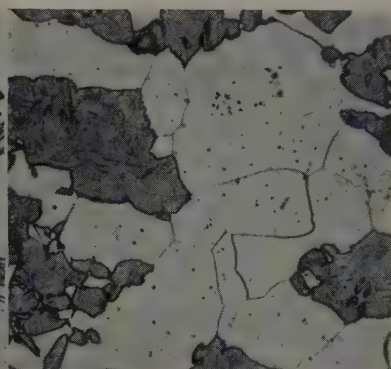


Fig. 12—Test No. 287.  $\alpha$ - $\gamma$  steel, recrystallized.

Same alloy as Test No. 283. Forged to 20 pct cross-section, annealed at 1000°C for 30 min and quenched. Nital etch. X500. Area reduced approximately 33 pct for reproduction.



cases the liquid/iron interfacial energies are similar and slightly over one half of the iron/iron energy, see Table X. A direct comparison may not be made between the intergranular energy of the  $\alpha$  and  $\gamma$  iron from this data, however, because the liquid/solid interfaces are not identical in each case.

Some alloying elements appear to have an effect upon the shape of the sulphide liquids between the iron grains. The sulphide liquid in the high silicon  $\alpha$ - $\gamma$  alloy described previously, Fig. 10, showed relatively high interfacial energies with the two iron phases. The energies were approximately two thirds that of the  $\alpha/\alpha$  or  $\gamma/\gamma$  intergranular energy. Likewise, Sims<sup>30</sup> found microstructures which might be interpreted to result from higher liquid/iron interfacial energies in steels which were silicon-killed.

**Metal Liquids:** Liquid copper will infiltrate into iron compacts<sup>21</sup> and will form a relatively small dihedral angle between iron grains. These features have been assigned to the interfacial energy relationships. The solubility of iron in copper does not increase markedly under 1250°C.<sup>14</sup> Consequently, it may be anticipated that the energy of the liquid-copper/ $\gamma$ -iron interface is relatively constant be-

Table X. Relative Interfacial Energies of Liquid Sulphide-Telluride\*/Iron Interfaces

| Test | Temperature, °C | Dihedral Angle Liquid vs. Fe/Fe | Liquid/Iron Interfacial Energy |
|------|-----------------|---------------------------------|--------------------------------|
| 144  | 890             | 20°                             | 0.50 <sub>7</sub>              |
| 265  | 1028            | 25°                             | 0.51 <sub>2</sub>              |

\*S = Te (atomic percent)

low that temperature. This was observed to be true on the basis of dihedral angles which were formed, Tables V and VI.

An addition of silver to liquid copper materially increases the liquid/iron interfacial energy until, in silver-rich liquids, the dihedral angle is near 180°. Likewise liquid lead, bismuth, and cadmium form dihedral angles between iron grains which are near 180°, indicating that the liquid/iron interfacial energy is relatively large. Iron is essentially insoluble in all of these liquids.

The difference in energies of the copper/iron and silver/iron interfaces cause the contact angles which these two liquids make with iron surfaces to differ. Molten copper has a 0° contact angle against iron in hydrogen. Molten silver has a contact angle of approximately 90°. From these relationships, it may be assumed that the surface energy of  $\gamma$  iron is approximately the same as the iron/silver interfacial energy and equal to, or greater than, the sum<sup>5</sup> of the iron/copper interfacial energy and the surface energy of liquid copper.†

#### Movement of Iron Interfaces

Smith<sup>4</sup> suggests three possible methods by which an interface between two phases may move to approach an equilibrium shape. 1—The atoms of one phase may diffuse through the other phase from positions of high surface energy to positions of lower

† By making the broad assumption that iron does not alter Sauerwalds<sup>22</sup> value of 1120 ergs per cm<sup>2</sup> for the surface energy of molten copper, a rough estimate for the minimum value for the surface energy of copper-saturated iron would be 1550 ergs per cm<sup>2</sup>.

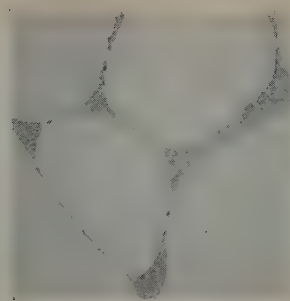


Fig. 13—Test No. 277. Iron sulphide liquid in iron oxide-free iron.

Annealed at 1325°C for 30 min and quenched. X500. Area reduced approximately 33 pct for reproduction.

surface energy. 2—This diffusion may proceed along the interface rather than through an adjacent phase. 3—The interfacial energies are sufficient to deform plastically the materials into shapes of minimum surface energies.

The diffusion processes appear to be the more significant methods of interfacial movement in the liquid-iron systems studied. For example, the energies associated with the liquid-silver/iron or liquid-cadmium/iron interface are relatively high as shown by the large dihedral angles they form between iron grains. Yet with these higher energies, the silver/iron interfaces did not readily conform to equilibrium shapes, as shown in Fig. 16. Likewise, angular iron grains in liquid cadmium did not spheroidize by plastic deformation. At the same temperature, the interface between iron and an iron sulphide liquid conformed readily to the interfacial forces although the energy of the interface was relatively low, as shown in Fig. 17. The iron must be dissolved and reprecipitated through the liquid phase or along the liquid interface to move the interface.

The grain boundaries in iron appeared to be influenced by the presence of iron oxide inclusions, Fig. 18. Three times as many inclusions were observed on the convex side of the  $\alpha$ -iron boundaries as on the concave side, as given in Table XI. The convex side would be behind the grain boundary if the grain boundaries may be assumed to move toward their center of curvatures.<sup>9</sup> Presumably the grain boundary moved forward more rapidly when it first came in contact with the inclusion, because

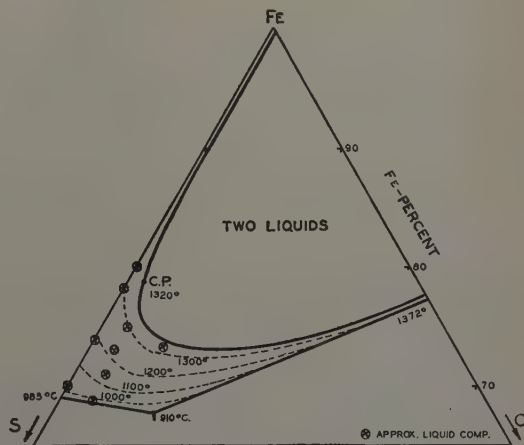


Fig. 14—Liquidus surface of the Fe-FeS-FeO system.<sup>18, 19</sup>

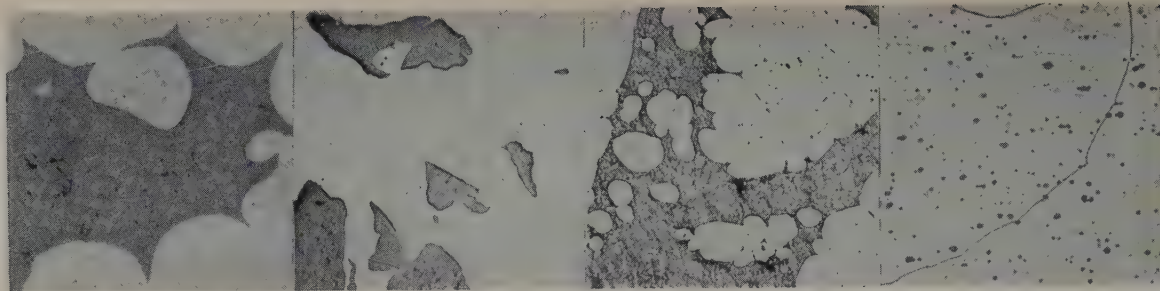


Fig. 15—Test No. 276. Iron sulphide-iron oxide liquid in iron.

Sulphur/oxygen = 8/2. Annealed at 1325°C for 30 min and quenched. X500. Area reduced approximately 33 pct for reproduction.

Fig. 16—Test No. 280. Liquid silver and  $\gamma$ -iron interfaces.

Annealed at 1000°C for 30 min and quenched. X200. Area reduced approximately 33 pct for reproduction.

Fig. 17—Test No. 75. Liquid sulphide and  $\gamma$ -iron interfaces.

Annealed at 1000°C for 30 min and quenched. X200. Area reduced approximately 33 pct for reproduction.

Fig. 18—Test No. 109. Boundary between  $\alpha$ -iron grains which contain iron oxide inclusions.

Iron oxide = 1.0 vol pct. Wire drawn and annealed at 885°C for 10 hr. X125. Area reduced approximately 33 pct for reproduction.

the curvature of the surface became much sharper as the boundary assumed a position essentially normal to the inclusion surface. When the boundary, as a whole, moved beyond the inclusion, the curvature in the immediate vicinity of the inclusion was first decreased and then reversed. As such, the boundary was halted locally, leaving the majority of the grain boundary inclusions in the observed positions. The austenitic grain growth inhibition in steels, which is attributed to alumina inclusions,<sup>23</sup> quite possibly results from this type of boundary retention. There the inclusion size is markedly smaller. As a result the grain growth is controlled by a relatively small inclusion volume.<sup>24</sup>

### Summary

The energy of the  $\gamma$ -iron grain boundary was determined, and the microstructures of iron containing several metallic and nonmetallic phases were examined with an attempt to interpret some of the observed structures in terms of the interfacial energy relationships.

To determine the energy of the  $\gamma$ -iron grain boundary, the interfacial energy between liquid copper and liquid copper sulphide was measured from the differential depression of their interface in two capillary tubes of unequal radii. The liquid copper/ $\gamma$ -iron, liquid copper sulphide/ $\gamma$ -iron, and  $\gamma$ -iron/ $\gamma$ -iron interfacial boundaries were then calculated from the dihedral angles—Fe vs. Cu/Cu<sub>2</sub>S, Cu vs. Fe/Fe, and Cu<sub>2</sub>S vs. Fe/Fe.

In addition to the differential depression of the menisci, which was determined by radiography, the densities of the two liquids, and the radii of curvatures of the menisci were required for the calculation of the energy of the two-liquid interface. The densities were measured from the pressures required to bubble nitrogen through the liquids. The radii of interfacial curvatures were calculated from the capillary radii by using Sugden's treatment of

Bashforth and Adams' tables. The dihedral angles used were those most frequently observed in the microsection of a quenched sample.

The energy of the iron-saturated, two-liquid interface is 100 ergs per cm<sup>2</sup> at 1105°C, dropping to approximately 70 ergs per cm<sup>2</sup> at 1200°C. This decrease may be extrapolated to zero near the critical temperature slightly above 1400°C. At 1105°C, the following interfacial energies involving iron were established: Liquid copper/liquid copper sulphide, saturated with Fe, 100 ergs per cm<sup>2</sup>; liquid copper/ $\gamma$  iron, 430 ergs per cm<sup>2</sup>; liquid copper sulphide/ $\gamma$  iron, 470 ergs per cm<sup>2</sup>;  $\gamma$  iron/ $\gamma$  iron, saturated with Cu and S, 850 ergs per cm<sup>2</sup>.

In a duplex,  $\alpha$ - $\gamma$ , iron-silicon alloy the energy of the  $\alpha$ -iron grain boundary was observed to be 0.9 that of the  $\gamma$ -iron boundary. In an iron-copper alloy, the above value was 0.85. In the former alloy, the energy of the  $\alpha/\gamma$  boundary was 0.7 that of the  $\gamma$ -iron boundary.

The interfacial energy between  $\gamma$  iron and a sulphide liquid was a little greater than 0.5 that of the  $\gamma$ -iron/ $\gamma$ -iron energy at 1000° to 1200°C. Above 1200°C, the liquid-iron interfacial energy dropped to less than 0.5. When oxygen was present with sulphur in the liquid this relative energy did not drop to less than 0.5. Thus a noticeable difference in microstructure resulted because the liquid spread less extensively between the iron grains in the latter case.

Evidence is given showing that the movement of the solid/liquid interfaces in compliance with the interfacial energy results from diffusion, either through the liquid or along the phase boundary, and not from the plastic deformation of the solid.

Some evidence is given to show the manner by which inclusions in iron act as grain growth inhibitors.

### Acknowledgments

A large share of the work required for this study was done as an employee of Carnegie-Illinois Steel Corp. This was made possible through the efforts of E. W. Pierce and B. R. Queneau of South Works. All of this is gratefully appreciated. The generous guidance of C. S. Smith and the stimulating discussions with him and others of the Institute for the Study of Metals were indispensable. The facilities of both the Institute and South Works were made available.

Table XI. Location of Inclusions on Grain Boundaries

| Location               | Number Observed |
|------------------------|-----------------|
| Convex side (Fig. 24)  | 227             |
| Concave side           | 74              |
| Approximately centered | 211             |
| Straight boundaries    | 140             |



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## Technical Note

# Precipitation and Diffuse Scattering in an Fe-Mo-Co Alloy

by A. H. Geisler and F. E. Steigert

THE permanent magnet alloy comol, which contains 17 pct Mo, 12 pct Co, balance Fe, exhibits a precipitation reaction analogous to that at the iron end of the binary Fe-Mo system. The equilibrium precipitate, ( $P_s$ ), has a structure isomorphous with  $Fe_3Mo_8$  which is rhombohedral with parameters  $a = 8.97\text{\AA}$  and  $\alpha = 30^\circ 38.6'$  according to the work of Arnfelt and Westgren.<sup>1</sup> In the ternary alloy the parameters are  $a = 8.87\text{\AA}$  and  $\alpha = 31^\circ 0.5'$ . Oscillating crystal patterns of a single matrix crystal,  $M$ , in which  $P_s$  was precipitated by slow cooling from  $1300^\circ\text{C}$ , showed that the orientation relationship of the two lattices is as follows:

$$(\bar{1}\bar{1}0)_{P_s} // (110)_M$$

$$(11\bar{1})_{P_s} // (\bar{1}\bar{1}0)_M$$

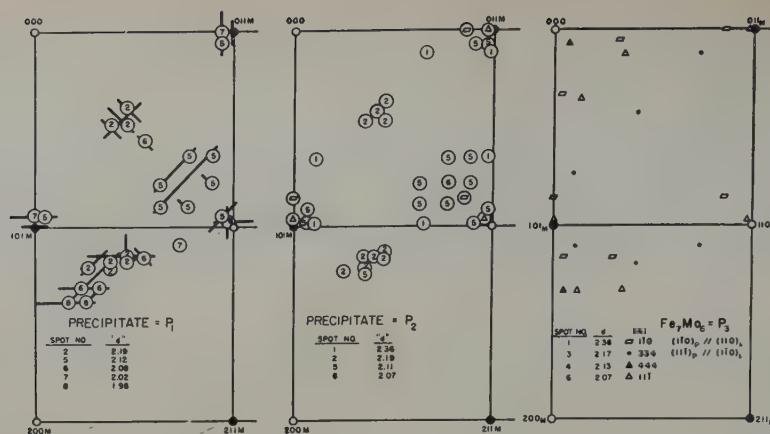
There are crystallites of  $P_s$  in 12 different orientations in a single crystal of the parent solid solution. Microscopic examination shows that the crystallites are generally plate-like with their lateral dimensions parallel to  $\{110\}$  matrix planes.

When precipitation in a supersaturated alloy

quenched from  $1300^\circ\text{C}$  progressed isothermally at temperatures between  $600^\circ$  to  $800^\circ\text{C}$ , the evolution of the  $P_s$  structure could be traced. Diffuse diffraction effects in Laue patterns provided early evidence of the precipitation process. Analyses of these by a previously described technique<sup>2</sup> showed that they corresponded to rod-like elements parallel to  $\langle 110 \rangle$  matrix directions in reciprocal space. With further aging to promote growth of the precipitate, the rod-like elements contracted to points in reciprocal space for normal Bragg reflection from the precipitate as shown by the left diagram in Fig. 1. Thus the diffuse scattering was attributed to the small thickness of the plate-like particles which was inadequate for sharp diffraction. When the precipitate particles were first thick enough to give normal diffraction their structure was different from that of the equilibrium precipitate,  $P_s$ . The first structure,  $P_1$ , presumably is a coherent transition struc-

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ture, for some of the rods pass through the (101) type points for the matrix showing that a precipitate reflection coincides with the (101) reflections and there are planes in  $P_1$  which have the same spacing as  $d_{101M}$ . Spacings of other planes in  $P_1$  are listed in Table I. Magnetic and mechanical hardening occur during the formation of  $P_1$ .

The coherent precipitate,  $P_1$ , subsequently transforms into a second structure,  $P_2$ , with interplanar spacings that resemble somewhat those of the  $\sigma$ -FeMo phase<sup>3</sup> as shown by the comparison of lines for  $\sigma$ -FeMo with those for specimens aged 18 hr at 700°C, or air cooled from 1300°C in Table I. There are certain similarities of the precipitates  $P_1$  and  $P_2$  which suggest that the second could form by simple readjustments of the first. Reflections Nos. 2 and 5 are common to the two. The structures are differentiated, however, by the slight splitting of the No. 5 reflection near  $(011)_M$  in the center diagram of Fig. 1 and by the absence of the two strong reflections

Nos. 1 and 6 near the  $(011)_M$  type reflections in Fig. 1. On the other hand, these two reflections for  $P_2$  agree with the  $(1\bar{1}0)$  and  $(11\bar{1})$  reflections for  $\text{Fe}_7\text{Mo}_6$ , the equilibrium precipitate,  $P_3$ , at the right in Fig. 1. The second precipitate, however, is differentiated from  $P_3$  by the presence for the former of the No. 5 reflection and the absence of the No. 3 reflections. The equilibrium precipitate,  $\text{Fe}_7\text{Mo}_6$ , forms during aging at the higher temperatures either isothermally or during slow cooling.

A proposed crystallographic mechanism of precipitation in this alloy awaits the solutions of the coherent structure and the sigma phase.

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Table 1. Interplanar Spacings for Precipitates in Comol

| Line No. | Precipitate = $P_1$ | Precipitate = $P_2$ |            |                |              | Precipitate = $P_3$ |             |                                 |              |       |
|----------|---------------------|---------------------|------------|----------------|--------------|---------------------|-------------|---------------------------------|--------------|-------|
|          | 1 Hr, 700°          | 18 Hr, 700°         | Air Cooled | $\sigma$ Fe-Mo | Intensities* | 18 Hr, 800°         | Slow Cooled | Fe <sub>7</sub> Mo <sub>6</sub> | Intensities* | hkl   |
| 1        |                     | 2.37                | 2.36       | 2.35           | W            | 2.37                | 2.36        | 2.37                            | VS           | (110) |
| 2        | 2.19                | 2.19                | 2.19       | 2.21           | VS           |                     |             |                                 |              |       |
| 3        |                     |                     |            |                |              | 2.17                | 2.17        | 2.17                            | S            | (334) |
| 4        |                     |                     |            |                |              |                     | 2.13        | 2.14                            | M            | (444) |
| 5        | 2.12                | 2.12                | 2.11       | 2.13           | M            |                     |             |                                 |              |       |
| 6        | 2.08                |                     | 2.07       | 2.08           | M            | 2.08                | 2.07        | 2.08                            | M            | (111) |
| 7        | 2.02                |                     |            | 2.04           | S            |                     |             | 2.03                            | S            | (443) |
| 8        | 1.98                |                     | 1.98       | 1.99           | VS           | 1.98                |             |                                 |              |       |
| 9        |                     |                     |            | 1.93           | M            |                     | 1.95        | 1.95                            | M            | (220) |
| 10       |                     |                     |            | 1.90           | VW           |                     | 1.90        | 1.91                            | M            | (113) |
| 11       |                     |                     |            | 1.82           | VW           |                     |             |                                 |              |       |
| 12       |                     |                     |            |                |              | 1.80                | 1.82        | 1.83                            | W            | (234) |
| 13       |                     |                     |            |                |              |                     | 1.78        | 1.78                            | W            | (331) |
| 14       |                     |                     | 1.37       | 1.37           | M            |                     | 1.73        | 1.73                            | W            | (224) |
| 15       |                     |                     |            |                |              |                     | 1.37        | 1.35                            | M            | (121) |
| 16       |                     | 1.31                | 1.31       | 1.30           | S            | 1.32                | 1.33        | 1.33                            | S            | (235) |
| 17       |                     |                     |            |                |              |                     | 1.30        | 1.31                            | M            | (114) |
| 18       | 1.283               |                     |            |                |              |                     | 1.290       | 1.297                           | M            | (542) |
| 19       |                     | 1.274               | 1.276      | 1.28           | VS           | 1.286               | 1.285       |                                 |              |       |
| 20       | 1.257               | 1.258               | 1.256      | 1.246          | W            |                     |             | 1.276                           | W            | (466) |
| 21       |                     |                     | 1.233      |                |              | 1.251               |             |                                 |              |       |
| 22       |                     |                     |            | 1.220          | M            |                     | 1.233       | 1.237                           | VW           | (225) |
| 23       |                     | 1.188               | 1.185      | 1.177          | M            | 1.225               | 1.217       | 1.227                           | VW           | (643) |
| 24       |                     | 1.091               | 1.082      | 1.100          | M            | 1.187               | 1.184       | 1.191                           | S            | (220) |
| 25       |                     |                     |            | 1.068          | VS           | 1.090               | 1.087       | 1.092                           | M            | (686) |
| 26       |                     |                     |            | 1.035          | VS           | 1.043               | 1.040       | 1.045                           | S            | (541) |
|          |                     |                     |            |                |              |                     | 1.024       | 1.031                           | S            | (632) |

\* VS—very strong. S—strong. M—medium. W—weak. VW—very weak.



# Desulphurizing Molten Iron with Calcium Carbide

by S. D. Baumer and P. M. Hulme

IN the late thirties, the National Carbide Co. co-operated with C. E. Wood, of the U. S. Bureau of Mines, in his investigation of the relative merits of various desulphurizers, including soda ash, caustic soda, and calcium carbide. Laboratory tests showed that carbide, when it could be made to react, is an excellent desulphurizing agent for molten iron. Sulphur content can be driven to lower levels and higher extractions obtained with carbide than with any of the more common reagents. Wood's results<sup>1</sup> are shown in Table I.

Unfortunately, as the Handbook of Cupola Operation puts it, the chemical fact that carbide is a good desulphurizer was of only academic interest because it was found to be extremely difficult to devise a practical means to make it react with molten iron. Calcium carbide is formed in the electric furnace at 4000°F and above, and its softening point is probably at least 500°F above the usual working temperatures encountered in iron and steel practice. Consequently, carbide does not form a true slag but floats as a dry powder on top of the metal and only a very small portion of it ever comes in actual contact with the iron. Stirring with a rabble, or pouring the metal over the carbide, increases the efficiency only slightly. Extractions of 20 to 30 pct can be obtained in this manner, but conventional soda slag treatment can do better than this and do it more cheaply.

All attempts to lower the melting point of carbide in order to obtain a reactive, liquid slag have so far proved fruitless. Directly under the arc in a metallurgical electric furnace, carbide becomes highly reactive. Excellent sulphur removal can be obtained without any slag other than a thin layer of carbide.<sup>2</sup> Similarly, good results are obtained by adding small amounts of carbide to the finishing slag in double-slag arc furnace practice.

To react a liquid with a solid, it is axiomatic that the liquid has to wet the solid before anything can happen. If the solid is heavier than the liquid, the problem is easy, but it becomes more difficult when the solid is much lighter than the liquid, as in the case of carbide and liquid iron. Wood recognized this problem and solved it in a unique fashion. The results shown in Table I were obtained by spinning the carbide beneath the surface of the molten iron by means of a refractory centrifuge. This technique allowed each particle of the finely divided carbide to come into intimate contact with the metal and to be wetted thereby.

Wood's centrifuge technique was successful in the laboratory where it achieved excellent and consistent results. Some attempts were made to expand this method to commercial practice, but serious difficulty was encountered in obtaining a refractory centrifuge head that would be economically feasible.

Table I—Crucible Tests with the Mechanical Dispersing Unit

| Test No. | Sulphur in Metal, Pct |              |                  | Sulphur Removed, Pct | CaC <sub>2</sub> , Lb per Net Ton | Wt of Charge, G | Lb of CaC <sub>2</sub> per Lb of S Removed* |
|----------|-----------------------|--------------|------------------|----------------------|-----------------------------------|-----------------|---------------------------------------------|
|          | Initial               | 2-Min Sample | Final from Ingot |                      |                                   |                 |                                             |
| 126      | 0.097                 | 0.007        | 0.007            | 92.7                 | 10                                | 1600            | 5.56                                        |
| 127      | 0.083                 | 0.012        | 0.009            | 89.2                 | 10                                | 1600            | 6.75                                        |
| 132      | 0.096                 | 0.027        | 0.019            | 80.2                 | 10                                | 1600            | 6.50                                        |

\* This column calculated from Wood's figures<sup>1</sup> shown in rest of table.

About this time the war intervened and the project lay dormant for several years.

In 1944, it was revived. It was suggested that the carbide could be blown into the metal with a carrier gas in an attempt to eliminate the necessity for the expensive and brittle centrifuge. The idea was first tried out in a fairly large ladle of iron using natural gas as the carrier. Considerable sulphur was removed, but it was quite obvious that the use of natural gas was not practical.

Attempts then were made to blow carbide into molten iron using, in turn, nitrogen, argon, carbon dioxide, air, and oxygen. The latter two gases proved unsatisfactory. Calcium evidently prefers oxygen to sulphur because in the tests calcium oxide and carbon dioxide were produced, the sulphur still being untouched in the iron. Nitrogen, argon, and carbon dioxide gave much better results, although the efficiencies and extractions were erratic, and only a few isolated tests approached the results obtained by Wood. Table II shows typical results obtained with these gases. The sulphur removals were interesting, sometimes even encouraging, but it is evident that such erratic behavior could not be tolerated in commercial practice.

A number of different types of equipment, such as sand blasting machines, refractory guns, and the like were used to blow the solid into the metal. All types required relatively large quantities of gas in order to maintain the flow of solid carbide through the system and into the metal. It was observed that the bubbles of gas breaking through the surface of the metal contained quantities of unreacted carbide. The liquid metal never came in contact with these particles and if it cannot wet them it cannot react with them.

The initial work had shown that carbide had great possibilities as a desulphurizer. In practice

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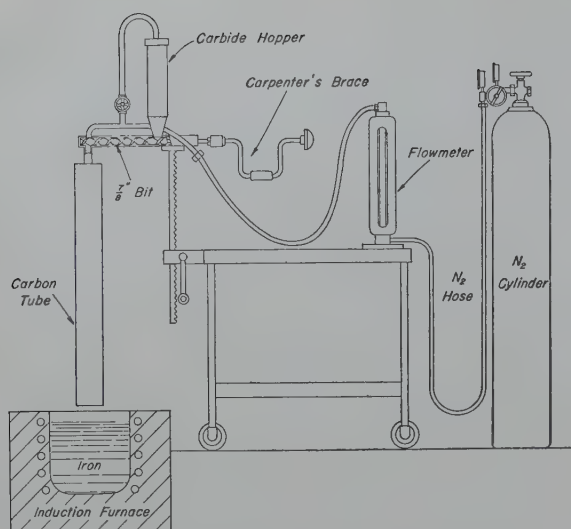


Fig. 1—Original screw feed carbide injection device.

the centrifuge method of injection could not be applied on an economical basis, but the blowing method showed definite possibilities, provided a method could be found to properly inject the carbide without the use of too much gas. With this consideration in mind, the real work of developing a process for using carbide as a desulphurizing agent in iron began.

### Apparatus Development

The first hand-operated apparatus, shown in Fig. 1, is merely a crude form of screw feed made from a carpenter's brace and bit and a few pieces of pipe. The apparatus was calibrated so that the weight of carbide delivered per revolution of the brace was known. Then, by counting the revolutions, it was possible to control the feed. Gas was introduced into the system at the end of the screw feeder and the flow controlled by a regulator and flowmeter. Carbon tubes of  $\frac{1}{2}$  in. ID were used for injection pipes.

Chateaugay pig, steel scrap, and iron sulphide were used to make up test heats which were melted in either a 100 or a 500-lb induction furnace. Analysis was adjusted to give an iron containing approximately 3.00 pct C, 0.150 S, 0.75 Mn, and 0.60 Si. When the metal was melted and the temperature reached 2650°F, any slag formed was skimmed off and the starting sample taken. The gas was started in the injection apparatus, the tube lowered into the metal and a predetermined amount of carbide injected into the melt.

The screw-feed method of introducing carbide enables the gas flow and the carbide flow to be independently controlled. It was found that particularly good results were obtained with only very light flows of gas. This is in marked contrast to the

blowing method which uses anywhere from 50 to 100 cu ft of gas per lb of carbide injected, as compared to as little as 0.25 cu ft per lb with the screw-feed method. With the screw-feed apparatus, crude as it was, results were obtained at once which compare in every way with those reported by Wood.

The next logical step was to put a small motor in place of the hand brace. After a few heats with this mechanized feeder, the present style feed mechanism was designed and built, as shown in Fig. 2. The principle is exactly the same as the hand-operated machine. The motor-operated screw is controlled by a Graham Variable Speed transmission capable of adjustment from 0 to 450 rpm. The whole mechanism can be raised or lowered by means of an air cylinder and can be rotated on a vertical axis through an arc of 150°. This was mounted between the 100 and 500-lb induction furnaces so that it could be used in either. The carbide hopper was placed directly on top of the feed mechanism above the sight-feed glass.

### Laboratory Results, 100 and 400-Lb Batches of Iron

Neither time nor resources were available to conduct a complete scientific research. The primary object of the laboratory work was to answer enough questions so that the pilot-plant stage could be started with some reasonable hope of success. The main question to be determined was: "Can 90 pct of the sulphur be removed from 3.00 pct carbon iron by means of calcium carbide on a basis which is economically competitive with other methods?" The results, Table III, indicate that it can be done.

Heat No. 96 was the first carbide heat using the hand feeder. At this stage it had not been learned how to salt the heat with sulphur to obtain high enough levels. However, it was quite encouraging to be able to take sulphur from 0.076 down to 0.005, a 93.5 pct extraction, in only 3 min. Three heats later, on heat No. 99, a phenomenal 98.7 pct extraction was obtained in 5 min with an expenditure of only 9.7 lb of carbide per lb of sulphur removed. During the course of this heat a most important point was observed. Injection time was 2.17 min and the sample taken directly after completion of injection analyzed 0.035 pct S. After waiting 5 min, the iron showed only 0.002 pct S.

Heat No. 100, not shown in the table, was run to test this. Carbide was injected at the rate of 1 lb per min for 1.5 min. A sample was then taken and the slag removed. This first sample showed a drop from the original 0.145 pct S to 0.045 pct S. After 2 min, a second sample analyzed 0.014 pct S and after 5 min, 0.008 pct S. At this time, there was some very light slag noticeable on the surface of the metal. This lead to the conclusion, which has subsequently been strengthened, that the calcium sulphide which is formed by dispersing carbide into the metal takes an appreciable time to float to the surface. Total sulphur is analyzed in the samples taken irrespective of whether it is in the form of iron or calcium sulphide. Therefore, although the reaction between the carbide and the sulphur is quite rapid, at least 8 to 10 min should be allowed after completion of injection in order to allow the metal to clear itself of the dispersed, finely divided calcium sulphide.

Heat No. 101 is interesting, not because the sulphur extraction is high, but because the starting sulphur is so high. Only 1 lb of carbide was injected and 130 points of sulphur removed at a ratio of 7.7 lb of carbide per lb of sulphur removed. On the next

Table II—Typical Results Using Carrier Gas Only  
Without Screw Feed

| Initial S | Final S | Pct Extracted | Wt of Metal, Lb | Lb CaC <sub>2</sub> , per Lb S Removed |
|-----------|---------|---------------|-----------------|----------------------------------------|
| 0.168     | 0.085   | 50.1          | 35,000          | 23.9                                   |
| 0.172     | 0.145   | 15.7          | 32,000          | 34.6                                   |
| 0.159     | 0.045   | 55.1          | 24,000          | 42.5                                   |
| 0.155     | 0.019*  | 92.7          | 27,000          | 13.1                                   |
| 0.161     | 0.071   | 55.8          | 31,000          | 56.1                                   |

\* Sample taken from bottom of ladle.



heat, No. 102, 217 points were removed with a ratio of 6.0 lb carbide per lb of sulphur.

The question then arose: "Would soda ash, given the same opportunity to contact the iron, give comparable results?" Heat No. 116 answers that question. Lime, caustic soda, and mixtures of lime, soda ash, carbide, and spar were tried in turn, with equally unsatisfactory results.

Up to this point, 100 lb had constituted the standard heat. However, in order to test whether size had any effect on the results, a number of 400-lb heats were run in the 500-lb induction furnace with the results shown in heats No. 122 through No. 124. Rates of feed were increased from 0.6 to 0.8 lb per min up to as high as 6 lb per min. The extractions were all better than 90 pct and the ratios of pounds carbide per pound sulphur removed were good.

A series of tests then were run to determine whether or not dilution of the carbide with cheaper, finely divided lime would prove more economical than straight carbide. The best result obtained is shown in heat No. 135. In this heat a good extraction was obtained but far more carbide was used to obtain it than would be necessary if carbide alone had been used.

The effect of adding ferromanganese to the mixture is shown in heat No. 143.

The 2-in. OD, ½-in. ID carbon tubes being used were very satisfactory for this test work where they withstood several immersions of 2 to 3-min duration. Obviously, however, this material is unsuited to commercial operations where immersion times would be far longer and even continuous. A number of refractory coverings were tried and the best apparently was Korundal, a high-alumina product, put out by Harbison-Walker Co. Heats No. 150 through No. 169 were run using this type tube. Heats No. 150 through No. 156 show that tube material has little, if any, effect on the results either on 100 or 400-lb batches. On heat No. 161, a return to the idea of lime dilution was made with good extraction but poor carbide-sulphur ratio.

### Pilot-Plant Development

After observing the laboratory work and the results obtained, officials of the American Tube and Stamping Plant Div. of the Stanley Works, Bridgeport, Conn., made facilities available for testing the process on a pilot-plant scale.

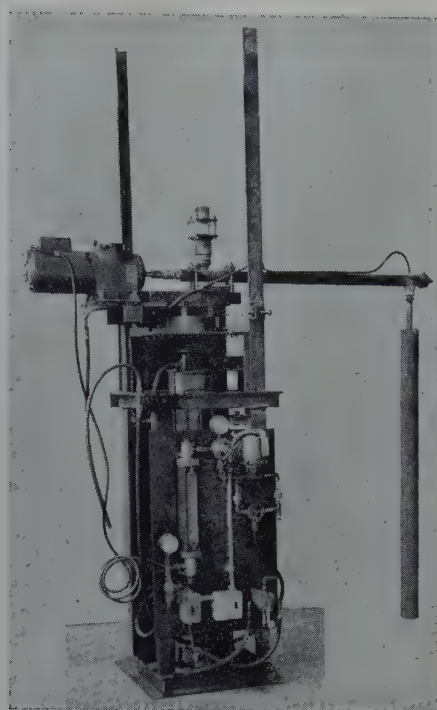


Fig. 2—Carbide feed injection apparatus.

At Bridgeport, hot metal for the open hearths is produced in 54-in. cupolas. There are two cupolas which operate on a 72 to 96-hr cycle. While one is producing, the other is being relined. Metal flows at the rate of 12 tons per hr through a front-slugging trap into a holding ladle from which it is transferred, as needed, to the open hearths.

Some consideration was given to treating the hot metal in the transfer ladle. The average quantity transferred per ladle is 35,000 lb which, at 0.150 pct, gives a total content of 62.5 lb of sulphur. In order to extract 90 pct, or 56.25 lb, 562.5 lb of carbide would be necessary. The injection equipment, already developed, delivered carbide at a maximum rate of 20 lb per min, which meant that it would take more than 28 min to make the injection; this, plus a 10-min wait to clear the metal of calcium sulphide, would give a total of 38-min tie-up of the ladle. To design an injection machine for more rapid flows was not advisable at this stage. Because of its pos-

Table III—Typical Laboratory Tests

| Heat No. | Wt of Metal, Lb | Desulphurizer                   |      | Feed Rate, Lb per Min | Sulphurs |        | Pct Extracted | Contact Time, Min | Desulphurizing 1 Lb S |
|----------|-----------------|---------------------------------|------|-----------------------|----------|--------|---------------|-------------------|-----------------------|
|          |                 | Type                            | Lb   |                       | Start    | Finish |               |                   |                       |
| 96       | 100             | CaC <sub>2</sub>                | 1.7  | 0.85                  | 0.076    | 0.005  | 93.5          | 3                 | 24.0                  |
| 97       | 100             | CaC <sub>2</sub>                | 1.5  | 0.65                  | 0.090    | 0.010  | 89.0          | 4                 | 18.75                 |
| 99       | 100             | CaC <sub>2</sub>                | 1.5  | 0.69                  | 0.157    | 0.002  | 98.7          | 5                 | 9.7                   |
| 101      | 100             | CaC <sub>2</sub>                | 1.0  | 0.62                  | 0.249    | 0.119  | 52.2          | 4                 | 7.7                   |
| 102      | 100             | CaC <sub>2</sub>                | 1.3  | 0.69                  | 0.277    | 0.060  | 78.4          | 10                | 6.0                   |
| 111      | 100             | CaC <sub>2</sub>                | 1.9  | 0.88                  | 0.137    | 0.021  | 84.5          | 10                | 12.9                  |
| 112      | 100             | CaC <sub>2</sub>                | 1.4  | 0.65                  | 0.139    | 0.027  | 80.5          | 3                 | 12.5                  |
| 116      | 100             | Na <sub>2</sub> CO <sub>3</sub> | 1.2  | 0.55                  | 0.132    | 0.100  | 24.2          | 10                | 37.6                  |
| 122      | 400             | CaC <sub>2</sub>                | 7.2  | 5.4                   | 0.154    | 0.007  | 95.5          | 10                | 12.2                  |
| 123      | 400             | CaC <sub>2</sub>                | 5.6  | 5.2                   | 0.136    | 0.006  | 95.5          | 10                | 13.3                  |
| 124      | 400             | CaC <sub>2</sub>                | 6.0  | 6.0                   | 0.152    | 0.008  | 93.5          | 10                | 10.8                  |
| 125      | 100             | CaC <sub>2</sub>                | 1.2  | 2.4                   | 0.184    | 0.014  | 92.5          | 10                | 7.1                   |
| 135      | 100             | CaC <sub>2</sub>                | 5.2  | 3.7                   | 0.168    | 0.008  | 95.5          | 10                | 32.5                  |
| 143      | 100             | CaC <sub>2</sub> 80 pct         | 3.18 | 3.7                   | 0.184    | 0.044  | 76.0          | 10                | 22.7                  |
|          |                 | CaO 20 pct                      |      |                       |          |        |               |                   |                       |
|          |                 | CaC <sub>2</sub> 72 pct         |      |                       |          |        |               |                   |                       |
|          |                 | CaO 18 pct                      |      |                       |          |        |               |                   |                       |
|          |                 | FeMn 10 pct                     |      |                       |          |        |               |                   |                       |
| 150      | 100             | CaC <sub>2</sub>                | 1.56 | 4.25                  | 0.178    | 0.005  | 97.2          | 10                | 9.0                   |
| 151      | 100             | CaC <sub>2</sub>                | 1.94 | 4.7                   | 0.176    | 0.018  | 89.9          | 10                | 12.3                  |
| 156      | 400             | CaC <sub>2</sub>                | 7.16 | 4.25                  | 0.188    | 0.009  | 95.0          | 10                | 10.0                  |
| 161      | 100             | CaC <sub>2</sub> 90 pct         | 3.06 | 3.34                  | 0.164    | 0.007  | 95.6          | 10                | 19.5                  |
|          |                 | CaO 10 pct                      |      |                       |          |        |               |                   |                       |

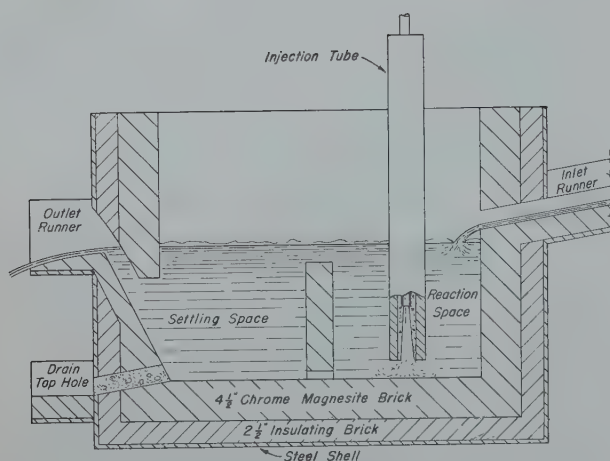


Fig. 3—Sketch of 1700-lb desulphurizing forehearth.

sible effect on needed production, all idea of carrying out test work in transfer ladle was abandoned.

It was decided to attempt to desulphurize the metal continuously as it left the cupola slag trap. A forehearth was installed parallel to the runner carrying the metal from the trap to the holding ladle; the stream of molten metal could be split to bypass a portion of the iron through this forehearth where it could be treated with carbide continuously by the same equipment used in the laboratory. The proportions of the forehearth were calculated to allow settling time for the calcium carbide to clear the metal. At the full rate of flow the capacity should be 4000 lb. This proved to be too large to fit into the available space. The largest forehearth which could be installed without interfering with production held 1700 lb. However, in order to get the information necessary, it was decided to build the 1700-lb forehearth although it was 15 pct too small to allow clearance of all the calcium sulphide formed in the reaction at metal flows of 6 tons per hr.

Fig. 3 shows a sketch of the forehearth, and Fig. 4 shows its position in relation to the cupola. It was a rectangular box made of  $\frac{1}{2}$ -in. welded steel plate, lined with  $2\frac{1}{2}$  in. of insulating brick next to the shell and faced with  $4\frac{1}{2}$  in. of chrome-magnesite brick in direct contact with the molten metal. The hearth area was 1 ft wide x 3 ft long, and the depth of metal was 15 in. at full 6 tons per hr flow. The hearth was divided by a submerged baffle into two

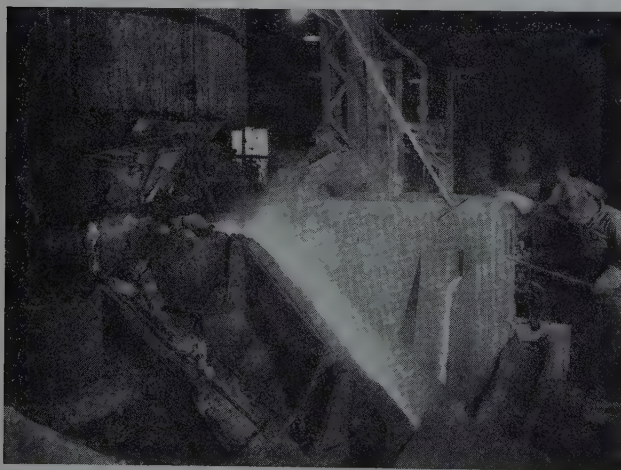


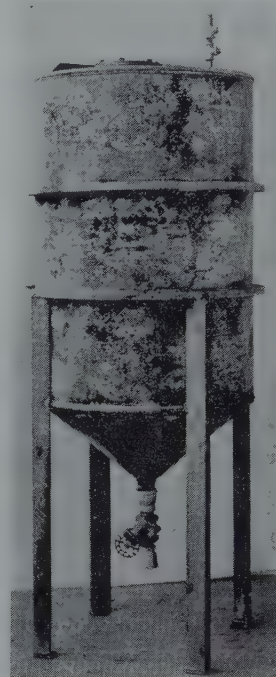
Fig. 4—Showing forehearth position with relation to cupola, slag trap, and runners.

sections. The untreated metal from the cupola runner flowed into the hearth on one side of this baffle where the injection of the fine carbide took place. The incoming metal and the churning action of the injected gas and carbide created considerable turbulence in this section, which gave the metal every opportunity to contact the solid carbide particles. The metal and the resulting slag rose and flowed over the dividing baffle to the outlet and skimming section of the hearth. Here the body of metal was relatively quiet and the solid particles of slag and calcium sulphide had an opportunity to float to the surface where they were skimmed off. The clean metal flowed out of the forehearth through a "teapot" spout which drew the metal from near the bottom of this section.

The whole forehearth was heated to working temperature before starting operations, but no firing was necessary after the full flow was attained.

A 1000-lb capacity carbide hopper, Fig. 5, was located between the cupolas on the charging floor level. Carbide flowed by gravity through a 2-in. gate

Fig. 5—A 1000-lb carbide hopper.



valve, and a 2-in. hose to the sight-feed glass above the screw-feed mechanism. A nitrogen atmosphere was maintained at about 8 psi maximum on the carbide hopper. This served both to keep the carbide dry and to balance the gas pressure in the entire system when the injection tube was immersed.

The injection tubes were made up as shown in Fig. 6. An extra-heavy-walled, welded 1-in. ID steel pipe served as the inner tube. To protect this working tube from metal and slag attack, it was fitted with refractory tubes similar to stopper rod sleeves. These were cemented in place by plastic chrome ore. The flared outlet nozzle was found essential to prevent bridging and plugging of the tube. The screw feeder was fitted with a revolution counter. The screw delivered a definite quantity per revolution, therefore the counter measured the pounds of carbide feed directly. The rate of feed was adjusted by means of the control wheel on the Graham Variable Speed Drive.

From the beginning of operations of the pilot plant, the chemistry compared favorably with the



batch operations on a laboratory scale. The basic figure of 10 lb of carbide per lb of sulphur removed was confirmed and while none of the continuous runs reached sulphur levels in the double "0" range, the 0.01 to 0.02 pct range was easily maintained. Because the forehearth was overloaded, it was felt that this caused some carry-over of calcium sulphide and that a larger hearth would produce lower sulphur levels and higher carbide efficiencies.

A typical run is shown in Fig. 7. At the start of the injection of carbide, there is 1700 lb of iron resident in the forehearth containing 0.176 pct S. The treatment begins to remove the sulphur from the metal and transfer it to the slag. At the same time, new metal containing 0.176 pct S is entering the system, and treated metal is leaving it at the same rate. As a result the sulphur comes down rapidly at first and gradually slows down, until a level of sulphur content is reached, where the rate of sulphur removal just balances the new sulphur coming in with the untreated metal. The rate at which this equilibrium can be reached is increased by increasing the carbide feed at the start of operations and then cutting back on the carbide feed until it is just sufficient to balance the incoming sulphur.

Fig. 8 shows how this is accomplished and also the effect of maintaining the balanced carbide feed

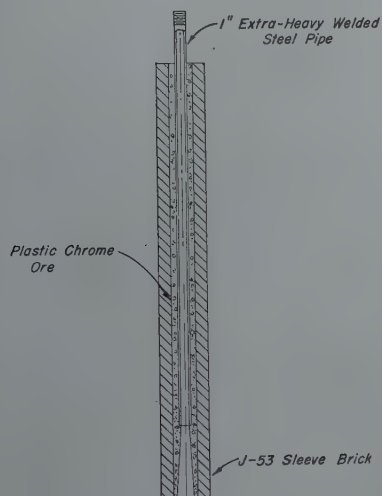


Fig. 6—Sketch of injection tube.

while increasing the rate of metal flow. As expected, the sulphur in the outgoing metal rises to a higher level. Naturally, therefore, when the metal flow is increased after balance is reached, the carbide feed rate must be increased in order to balance the sulphur at the desired low level.

The major difficulties were either mechanical or physical. It took considerable effort to evolve the relatively simple injection tube used. In the laboratory, carbon tubes of uniform bore had been used, but these would not stand more than 5 or 10 min of continuous immersion.

All refractory-covered tubes plugged after a few minutes immersion until the trick of flaring the exit end was discovered. Numerous types of refractory cover were tried, including graphite, clay-graphite, chrome, magnesite, mullite, zirconia, and clay. The best found was a fairly high silica clay, which is relatively cheap, stands the heat shock of immersion, and will last continuously in contact with the carbide slag from 4 to 5 hr. Changing a tube is a rapid and simple process so, while better tubes may be forthcoming at some future date, they will have to be really remarkable in their lasting powers to

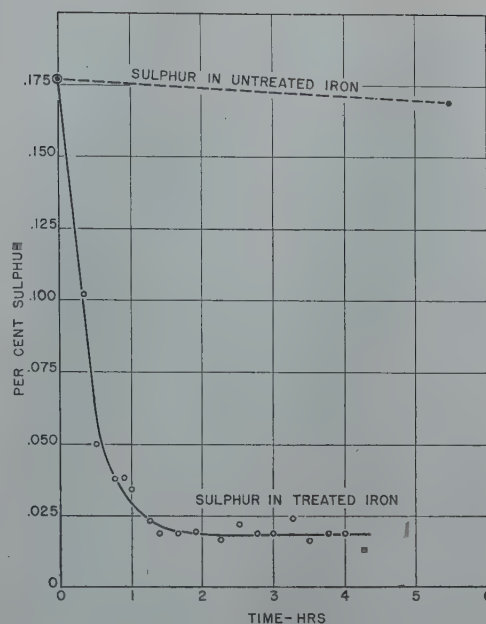


Fig. 7—Typical pilot-plant run.

complete economically with the cheap clay tube. Fig. 9 shows a tube injecting carbide into the molten iron.

The slag formed was dry, crumbly, and quite voluminous. It did not run off even though its level was a number of inches above the skimming breast. It had to be dragged out mechanically. All attempts to add fluxing agents, such as spar, borax, etc., to the slag caused immediate and serious reversion of the sulphur to the metal. The slag, at first, was pulled off by hand rabbles into cast iron pots. Eventually, an air-operated rabble was built and the slag dragged off mechanically into a water trough which carried it to the slag dump-car. Fig. 10 shows the mechanical slagger in action, and Fig. 11 shows a general view of the entire pilot-plant assembly.

Trouble with the rabble heads was anticipated but it never materialized. When the slagging ma-

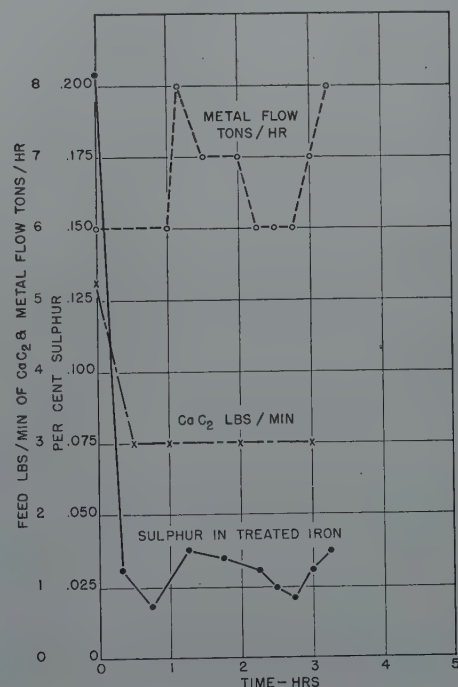


Fig. 8—Showing effect of increased feed rate at start and varying flow of iron.

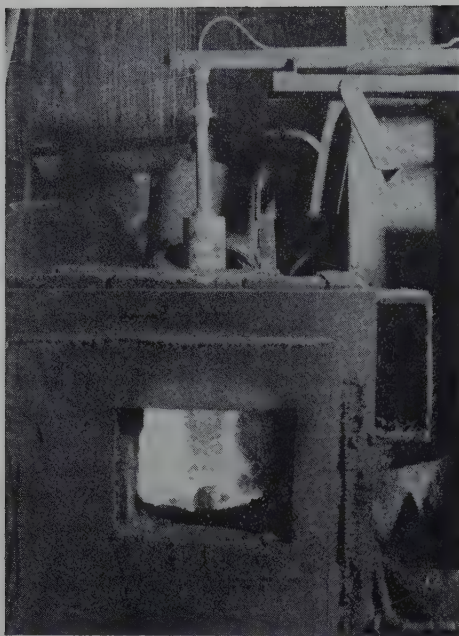


Fig. 9—Tube working injecting carbide into molten iron.

chine was adjusted so that the bottom edge of the blade cleared the surface of the metal by about an inch, a head made of 1-in. steel plate lasted for hours. A light clay wash prevented serious sticking of slag on the head and, if some did accumulate, it was easily taken off with a sharp blow of a hammer.

Demand of the open hearths for metal, and other cupola operating circumstances apart from the pilot operation, made it impossible to get continuous runs of more than 5-hr duration. As stated above, space was strictly limited so that the wall thickness of the forehearth was relatively thin. The temperature loss by radiation in the system was quite large, amounting to about 100°F when the metal was run through the forehearth without carbide treatment. After starting carbide injection, the temperature loss rose to about 120°F at the start, and fell to about 100°F again when equilibrium was reached. This loss was of little importance to the pilot investigation as long as the flow of metal could be maintained. However, when the cupola had to be shut down for lack of immediate demand by the open hearths, the treatment forehearth had to be drained because of danger of serious skulling. For this rea-

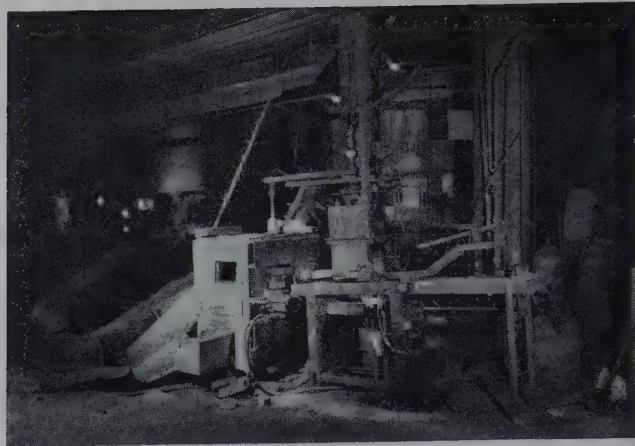


Fig. 11—View of entire pilot-plant assembly.

son, the duration of the pilot-plant runs was limited. Nevertheless, there appears to be no reason to doubt that the process can be operated continuously for indefinite periods, if the forehearth is properly designed and the metal flow is reasonably consistent.

### Conclusions

1—Calcium carbide can be made to desulphurize molten iron either on a batch or a continuous flow operation.

2—When properly applied, it can consistently extract better than 90 pct of the sulphur content.

3—About 10 to 12 lb of carbide is required per pound of sulphur removed.

4—There was no reversion of sulphur to the metal from the carbide slag except when attempts were made to change the composition of the slag.

5—The efficiency appears to be independent of the sulphur level in the metal, and also independent of the temperature of the metal, at least in the range 2550° to 2850°F.

6—The process is more expensive than the conventional soda treatments. The cost will be from \$0.75 to \$2.00 per ton of metal treated, depending on the quantity of sulphur to be removed.

7—The process will drive sulphur content to lower levels more consistently than the conventional treatments. Sulphur levels in the 0.01 to 0.02 pct range and lower are easily attainable even when the starting sulphurs are as high as 0.200 pct.

8—When sulphur levels in the 0.06 to 0.08 pct range are satisfactory in the treated iron, the process is not competitive with the conventional treatments on a straight cost basis. Below this range, however, it appears to offer real possibilities.

### Acknowledgment

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Fig. 10—Mechanical slagger in action.



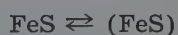
# Distribution of Sulphur Between Liquid Iron and Slags of Low Iron-Oxide Concentrations

by R. Rocca, N. J. Grant, and J. Chipman

**Desulphurization of liquid iron by reducing slags of the electric-furnace type was studied from 65 heats. Variations were made in basicity over a wide range and in FeO up to about 5 pct for their effects on desulphurization. The role of FeO in desulphurization from the blast furnace, to the electric furnace, to the oxidizing conditions of the open hearth is shown to fit a relatively simple pattern of behavior.**

THE mechanism which controls the desulphurization of molten iron by basic slags has been the object of several investigations. In particular, equilibrium determinations have been made both in the field of basic open-hearth slags, which have a high iron-oxide concentration, and in the field of blast-furnace slags which have a very low iron-oxide concentration. In both cases the desulphurization ratio has been found to increase with increasing basicity of the slags; however, the mechanism of desulphurization differs in the two cases.

In basic open-hearth slags desulphurization occurs mainly as a partition of iron sulphide:<sup>1</sup>



and the desulphurization ratio is approximately independent of iron-oxide concentration in the slag.

In blast-furnace slags the concentration of iron oxide is very low as a result of the highly reducing conditions in which they are formed. The controlling reaction for desulphurization is then:<sup>2, 3</sup>



The slags of the reducing stage in the electric furnace have an iron-oxide concentration which is intermediate between blast-furnace and open-hearth slags. The study of the mechanism of desulphurization for these slags has been the object of this investigation.

The importance of low (FeO) in the slag for desulphurization was first verified by Bardenheuer and Geller,<sup>4</sup> who found that high desulphurization ratios were obtained in highly reduced slags. It was recognized<sup>5, 6</sup> that iron oxide in the slag becomes a controlling factor in desulphurization only at FeO concentrations approximately under 5 pct. A recent

investigation conducted by Buehl,<sup>7</sup> upon the suggestion of one of the authors, confirmed this opinion from the results obtained from a heat conducted in a small arc furnace.

In the present investigation, slags of very high basicity, such as often are encountered in the basic electric furnace, could not be studied, but equilibrium data have been obtained for slags in a wide basicity range. The iron-oxide concentration in these slags ranged from 0.08 to 15 pct and was controlled by the addition of silicon to the metal. Other constituents of the slags were mainly CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaF<sub>2</sub>.

The experimental technique was essentially the same as that of previous investigations.<sup>1, 8-10</sup> In an open magnesia-lined induction furnace, 65 lb of Armco ingot iron was melted. An atmosphere of hydrogen was maintained over the melt for 1 hr to bring the carbon content down to approximately 0.010 pct maximum. The bath then was exposed to air for 25 min to remove hydrogen. The electrodes were put in place, and the furnace was operated from this point on in an atmosphere of nitrogen. A synthetic slag was added to which additions of silicon and iron sulphide were made. A rate study conducted at the beginning of this investigation had

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Table I. Chemical Analysis

| Heat | Sample | Temperature, °C | Steel Sample |        |        |        | Slag Sample |                                |                  |       |       |                  |                                |
|------|--------|-----------------|--------------|--------|--------|--------|-------------|--------------------------------|------------------|-------|-------|------------------|--------------------------------|
|      |        |                 | Si           | O      | S      | (S)    | FeO         | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | CaO   | MgO   | CaF <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> |
| 58   | 2      | 1617            | 0.007        | 0.060  | 0.026  | 0.006  | 16.21       | 0.25                           | 40.56            | 3.32  | 31.10 | 4.93             | 1.06                           |
|      | 4      | 1626            | 0.007        | 0.060  | 0.027  | 0.005  | 13.41       | 0.29                           | 39.41            | 12.52 | 27.78 | 3.45             | 1.02                           |
|      | 6      | 1604            | 0.007        | 0.065  | 0.027  | 0.008  | 8.92        | 0.39                           | 31.80            | 15.56 | 30.25 | 8.35             | 1.10                           |
|      | 8      | 1638            | 0.007        | 0.063  | 0.026  | 0.009  | 8.57        | 0.53                           | 27.58            | 15.92 | 29.74 | 10.42            | 5.56                           |
|      | 10     | 1642            | 0.007        | 0.058  | 0.027  | 0.014  | 8.89        | 0.47                           | 22.32            | 19.32 | 32.12 | 9.90             | 4.76                           |
|      | 16     | 1588            | 0.007        | 0.055  | 0.028  | 0.005  | 11.74       | 0.53                           | 37.80            | 20.05 | 24.00 | 1.52             | 2.42                           |
| 59   | 2      | 1588            | 0.30         | —      | 0.006  | 0.005  | 2.34        | 0.11                           | 42.24            | 5.50  | 25.60 | 8.14             | 9.62                           |
|      | 4      | 1586            | 0.39         | 0.0084 | 0.005  | 0.004  | 0.77        | 0.02                           | 39.62            | 7.05  | 26.30 | 13.60            | 4.66                           |
| 60   | 5      | 1544            | 0.447        | 0.0066 | 0.055  | 0.011  | 1.74        | 0.05                           | 43.32            | 16.56 | 24.70 | 4.46             | 0.58                           |
|      | 10     | 1540            | 0.464        | 0.0060 | 0.072  | 0.009  | 1.61        | 0.04                           | 46.16            | 16.08 | 24.39 | 6.57             | 0.08                           |
|      | 14     | 1659            | 0.369        | 0.0073 | 0.051  | 0.017  | 1.13        | 0.02                           | 42.44            | 20.88 | 26.95 | 2.67             | —                              |
|      | 16     | 1688            | 0.390        | 0.0075 | 0.050  | 0.020  | 1.06        | 0.02                           | 41.86            | 17.34 | 29.58 | 6.00             | 0.58                           |
|      | 18     | 1619            | 0.490        | 0.0051 | 0.047  | 0.054  | 0.46        | 0.02                           | 38.36            | 20.11 | 31.80 | 3.47             | 0.44                           |
|      | 20     | 1657            | 0.646        | 0.0044 | 0.042  | 0.106  | 0.32        | —                              | 38.02            | 21.56 | 32.95 | 3.29             | 0.06                           |
|      | 22     | 1644            | 0.643        | 0.0044 | 0.066  | 0.260  | 0.29        | —                              | 38.00            | 22.67 | 32.45 | 3.78             | 0.32                           |
|      | 24     | 1619            | 0.628        | 0.0043 | 0.060  | 0.310  | 0.25        | —                              | 36.52            | 24.97 | 31.02 | 3.31             | 0.16                           |
| 63   | 6      | 1610            | 0.221        | 0.0041 | 0.037  | 0.144  | 0.20        | —                              | 31.58            | 14.33 | 37.61 | 14.50            | 1.34                           |
|      | 8      | 1634            | 0.210        | 0.0057 | 0.036  | 0.141  | 0.31        | —                              | 28.32            | 14.27 | 40.55 | 14.34            | 1.66                           |
|      | 10     | 1717            | 0.180        | —      | 0.036  | 0.128  | 0.58        | —                              | 27.02            | 14.79 | 42.39 | 12.99            | 1.76                           |
|      | 12     | 1682            | 0.317        | 0.0056 | 0.033  | 0.235  | 0.31        | —                              | 23.62            | 12.85 | 51.89 | 10.17            | 1.80                           |
|      | 14     | 1582            | 0.391        | 0.0038 | 0.028  | 0.313  | 0.15        | —                              | 27.04            | 17.40 | 28.27 | 15.10            | 1.34                           |
|      | 16     | 1572            | 0.377        | 0.0046 | 0.022  | 0.460  | 0.17        | —                              | 28.28            | 14.68 | 58.15 | 15.37            | 0.54                           |
|      | 20     | 1622            | 0.516        | 0.0043 | 0.034  | 0.123  | 0.25        | —                              | 25.68            | 13.35 | 39.71 | 17.51            | 2.28                           |
|      | 22     | 1642            | 0.508        | —      | 0.032  | 0.210  | 0.24        | —                              | 24.54            | 17.55 | 38.00 | 14.96            | 2.46                           |
|      | 34     | 1597            | 0.484        | 0.053  | 0.0053 | 0.250  | 0.33        | —                              | 26.16            | 14.22 | 41.09 | 14.75            | 2.86                           |
| 67   | 16     | 1634            | 0.005        | 0.0610 | 0.0706 | 0.260  | 3.65        | —                              | 1.50             | 8.99  | 6.35  | 76.33            | —                              |
|      | 18     | 1682            | 0.001        | 0.0604 | 0.0785 | 0.211  | 4.82        | —                              | 0.66             | 7.18  | 6.96  | 77.85            | 0.76                           |
|      | 20     | 1687            | 0.001        | 0.0420 | 0.0779 | 0.154  | 3.81        | —                              | 1.48             | 4.67  | 7.86  | 80.37            | 1.04                           |
| 68   | 2      | 1752            | 0.002        | 0.0181 | 0.128  | 0.045  | 4.04        | 0.03                           | 42.66            | 15.35 | 35.75 | —                | 1.94                           |
|      | 4      | 1702            | 0.006        | 0.0169 | 0.127  | 0.033  | 4.19        | 0.04                           | 42.38            | 16.55 | 33.08 | —                | 2.98                           |
|      | 6      | 1657            | 0.001        | 0.0145 | 0.129  | 0.0327 | 5.80        | 0.04                           | 44.86            | 15.44 | 30.30 | —                | 3.68                           |
|      | 8      | 1667            | —            | 0.0179 | 0.127  | 0.0339 | 4.59        | 0.03                           | 40.96            | 17.76 | 30.69 | —                | 4.59                           |
|      | 10     | 1612            | 0.066        | 0.0060 | 0.204  | 0.0927 | 1.23        | 0.01                           | 42.66            | 21.61 | 27.76 | —                | 5.32                           |
|      | 12     | 1647            | 0.021        | 0.0057 | 0.202  | 0.104  | 1.36        | —                              | 40.54            | 21.44 | 30.01 | —                | 5.80                           |
|      | 14     | 1657            | 0.004        | 0.0191 | 0.200  | 0.101  | 1.53        | —                              | 38.14            | 22.22 | 31.10 | —                | 6.96                           |
|      | 16     | 1652            | 0.002        | 0.0112 | 0.196  | 0.0701 | 2.54        | 0.02                           | 36.52            | 23.23 | 30.58 | —                | 6.70                           |
|      | 18     | 1652            | 0.01         | 0.0093 | 0.190  | 0.288  | 0.56        | —                              | 37.00            | 26.11 | 29.30 | —                | 7.16                           |
|      | 20     | 1662            | 0.01         | 0.0116 | 0.187  | 0.193  | 0.087       | —                              | 37.04            | 25.41 | 29.49 | —                | 7.24                           |
|      | 22     | 1647            | 0.01         | 0.0093 | 0.173  | 0.496  | 0.35        | —                              | 36.46            | 26.94 | 29.06 | —                | 7.06                           |
|      | 24     | 1657            | 0.01         | 0.0093 | 0.168  | 0.422  | 0.43        | —                              | 35.70            | 26.81 | 29.34 | —                | 7.58                           |
|      | 26     | 1702            | 0.083        | 0.0103 | 0.168  | 0.339  | 0.70        | 0.01                           | 34.22            | 25.25 | 31.75 | —                | 7.75                           |
| 69   | 4      | 1617            | 0.220        | —      | 0.057  | 0.160  | 0.25        | —                              | 38.26            | 18.35 | 36.11 | 7.09             | 0.25                           |
|      | 6      | 1654            | 0.398        | —      | 0.054  | 0.170  | 0.34        | —                              | 33.78            | 17.47 | 41.81 | 5.65             | 0.14                           |
|      | 8      | 1642            | 0.562        | —      | 0.048  | 0.230  | 0.54        | —                              | 23.12            | 10.94 | 53.67 | 11.15            | 0.24                           |
|      | 10     | 1642            | 0.641        | —      | 0.043  | 0.280  | 0.26        | —                              | 31.77            | 18.64 | 40.12 | 6.75             | 0.18                           |
|      | 12     | 1654            | 0.596        | —      | 0.061  | 0.420  | 0.35        | —                              | 23.91            | 14.43 | 49.90 | 10.79            | 0.48                           |
|      | 14     | 1629            | 0.686        | —      | 0.063  | 0.400  | 0.18        | —                              | 32.90            | 14.78 | 40.18 | 11.11            | 0.40                           |
| 70   | 16     | 1567            | 0.606        | —      | 0.055  | 0.570  | 0.08        | —                              | 36.90            | 19.31 | 31.91 | 10.70            | 0.40                           |
|      | 2      | 1582            | 0.183        | —      | 0.062  | 0.027  | 1.71        | —                              | 49.07            | 26.30 | 21.09 | —                | 0.34                           |
|      | 4      | 1554            | 0.336        | —      | 0.065  | 0.058  | 0.58        | —                              | 47.54            | 29.76 | 21.68 | —                | 0.36                           |
|      | 6      | 1684            | 0.494        | —      | 0.055  | 0.180  | 0.29        | —                              | 41.60            | 28.41 | 28.72 | —                | 0.52                           |
|      | 8      | 1697            | 0.632        | —      | 0.051  | 0.270  | 0.30        | —                              | 37.54            | 25.09 | 36.59 | —                | 0.30                           |
|      | 10     | 1682            | 0.708        | —      | 0.050  | 0.270  | 0.39        | —                              | 33.75            | 23.62 | 41.60 | —                | 0.32                           |
| 72   | 12     | 1642            | 0.676        | —      | 0.068  | 0.410  | 0.33        | —                              | 34.81            | 25.18 | 39.01 | —                | 0.38                           |
|      | 2      | 1642            | 0.31         | —      | 0.100  | 0.38   | 0.33        | —                              | 33.38            | 18.71 | 41.19 | 3.11             | —                              |
|      | 4      | 1674            | 0.28         | —      | 0.100  | 0.27   | 0.45        | —                              | 23.46            | 13.51 | 57.40 | 2.86             | —                              |
|      | 6      | 1652            | 0.55         | —      | 0.089  | 0.36   | 0.33        | —                              | 36.78            | 20.94 | 41.20 | 0.41             | —                              |
|      | 8      | 1674            | 0.55         | —      | 0.088  | 0.28   | 0.36        | —                              | 36.38            | 19.38 | 43.39 | —                | —                              |
|      | 10     | 1630            | 0.68         | —      | 0.085  | 0.28   | 0.23        | —                              | 43.40            | 25.29 | 31.33 | —                | —                              |
|      | 12     | 1672            | 0.60         | —      | 0.062  | 0.34   | 0.27        | —                              | 40.90            | 21.95 | 36.87 | —                | —                              |
|      | 14     | 1687            | 0.63         | —      | 0.082  | 0.32   | 0.25        | —                              | 38.80            | 21.12 | 40.33 | —                | —                              |
| 74   | 16     | 1619            | 0.76         | —      | 0.078  | 0.46   | 0.17        | —                              | 41.12            | 24.96 | 33.62 | —                | —                              |
|      | 4      | 1650            | 0.53         | —      | 0.068  | 0.30   | 0.30        | —                              | 33.38            | 24.19 | 40.10 | —                | —                              |
|      | 6      | 1647            | 0.70         | 0.0048 | 0.065  | 0.32   | 0.23        | —                              | 36.64            | 23.67 | 39.70 | —                | —                              |
|      | 8      | 1662            | 0.79         | —      | 0.065  | 0.29   | 0.29        | —                              | 37.88            | 21.61 | 40.74 | —                | —                              |
|      | 10     | 1642            | 0.78         | —      | 0.093  | 0.80   | 0.25        | —                              | 30.20            | 25.64 | 32.50 | —                | 10.58                          |
|      | 12     | 1630            | 0.78         | 0.0073 | 0.077  | 0.92   | 0.19        | —                              | 26.12            | 27.70 | 31.89 | —                | 13.60                          |
|      | 14     | 1622            | 1.11         | —      | 0.062  | 1.16   | 0.15        | —                              | 26.04            | 29.48 | 29.03 | —                | 15.34                          |
|      | 16     | 1622            | 1.09         | —      | 0.054  | 1.17   | 0.17        | —                              | 23.88            | 29.89 | 28.56 | —                | 16.88                          |
| 75   | 18     | 1642            | 1.27         | —      | 0.050  | 1.09   | 0.14        | —                              | 25.14            | 30.44 | 25.72 | —                | 18.34                          |
|      | 2      | 1614            | 1.74         | —      | 0.10   | 0.015  | 5.08        | Total Fe<br>As FeO             | 66.86            | 0.66  | —     | —                | —                              |
|      | 4      | 1554            | 0.51         | 0.0043 | 0.11   | 0.019  | 4.90        | —                              | 66.68            | 0.78  | —     | —                | —                              |
|      | 6      | 1554            | 0.76         | —      | 0.115  | 0.025  | 3.16        | —                              | 63.46            | —     | —     | —                | —                              |
|      | 8      | 1612            | 0.95         | —      | 0.105  | 0.017  | 2.81        | —                              | 66.70            | 0.87  | —     | —                | —                              |
|      | 10     | 1652            | 1.15         | 0.0076 | 0.105  | 0.016  | 2.85        | —                              | 66.70            | —     | —     | —                | —                              |
|      | 12     | 1622            | 1.02         | 0.0072 | 0.105  | 0.016  | 2.80        | —                              | 66.76            | —     | —     | —                | —                              |
|      | 14     | 1599            | 1.31         | 0.0066 | 0.103  | 0.034  | 2.10        | —                              | 63.30            | 0.65  | —     | —                | —                              |
|      | 16     | 1597            | 0.46         | —      | 0.107  | 0.021  | 1.88        | —                              | 64.16            | 0.65  | —     | —                | —                              |
|      | 18     | 1577            | 1.99         | 0.0036 | 0.13   | 0.026  | 1.48        | —                              | 64.92            | —     | —     | —                | —                              |
|      | 20     | 1590            | 2.15         | 0.0043 | 0.13   | 0.045  | 1.45        | —                              | 63.48            | 0.61  | —     | —                | —                              |
|      | 22     | 1603            | 2.20         | —      | 0.13   | 0.057  | 1.28        | —                              | 61.80            | 0.75  | —     | —                | 0.58                           |

Dash means not run.



shown that sulphur equilibrium was essentially approached within 30 min after the addition of iron sulphide, or after a change in the composition of the slag. Accordingly, samples were taken at 45 to 60 min intervals depending upon the apparent fluidity of the slag. Temperatures were measured just before sampling by means of tungsten-molybdenum thermocouples and are considered to be correct within 10°C. New additions to the slag or metal were made immediately after sampling, including silicon metal additions to maintain low oxidation values. All sampling was accomplished by the use of long-handled split steel molds of the type used in previous investigations.<sup>1, 8-10</sup>

The results of chemical analysis of the slag and metal samples are shown in Table I. All calcium present was calculated to CaO and CaF<sub>2</sub>.

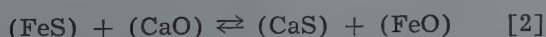
Some metallic iron was present in the slags and was separated by passing the slag sample over a Frantz iso-dynamic separator four or five times. The magnetic separator yielded better results than the determination of metallic iron by the copper sulphate method, the latter method accounting apparently for only a fraction of the metallic iron present. The analyses of chemically combined iron are reported in Table I as iron oxide, although they include any iron sulphide present in the slag. The analytical uncertainty is believed to be  $\pm 0.02$  pct FeO. Other analyses were by conventional methods.

Although the data obtained, reported in Table I, are of the same order of accuracy of previous investigations,<sup>1, 8-10</sup> it is felt that the errors involved are somewhat higher. One of the main controlling factors was iron-oxide activity of the slag. Such activity could not be measured from the oxygen concentration in the metal, since the oxygen values were very low, and of the same order of magnitude as the accuracy of the vacuum-fusion analyses ( $\pm 0.002$  pct). Hence a measure of the oxygen activity would come only from the evaluation of the iron-oxide concentration in the slag. Moreover, although the furnace atmosphere was controlled closely, small amounts of oxidation were unavoidable. The iron-oxide concentration in the slag was probably shifting slowly and might not have been in complete equilibrium with the metal, especially with the most basic, and less fluid slags. The constancy of the sulphur ratio, after the first 30 min following an addition, was evidence that the desulphurization reaction reasonably approached equilibrium, even if others, such as the slow silicon reaction, were often far from equilibrium.

### Analysis of Experimental Data

In the chemical analysis of the slags, Table I, calcium present in the form of calcium sulphide was included in the total concentration of lime and was, therefore, considered to act as a base.<sup>2, 3</sup>

The most widely accepted mechanism of desulphurization, under reducing conditions, is expressed by the following reactions:



resulting in the overall reaction:



$$K = \frac{(a_s) \cdot (a_{\text{FeO}})}{a_s \cdot (a_{\text{CaO}})} \quad [4]$$

The activity of sulphur in the slag can be assumed to be approximately proportional to its weight percent, for low concentrations. The activity coefficient of sulphur in iron, in the presence of silicon, has been determined by Morris and Williams<sup>11</sup> and their values have been employed here for the computation of  $a_s$ . A more difficult task is involved in the calculation of the activity of iron oxide and lime in the slag, since our present knowledge of the structure of molten slags is more of a qualitative than of a quantitative nature.

On the basis of a molecular approach, FeO and CaF<sub>2</sub> were assumed to be neutral species. The basicity of the slags was expressed by a molar ratio for rough grading of the slags, defined as:

$$b = \frac{(\text{CaO}) + (\text{MgO})}{(\text{SiO}_2) + (\text{Al}_2\text{O}_3)}$$

The slags reported in Table I were divided on the basis of the value of this ratio into acid slags ( $b < 1$ ) and basic slags ( $b > 1$ ). Since the basic slags ranged in basicity from  $b = 1$  to  $b = 4$ , it was felt that two different calculation bases must be employed for the more basic and less basic slags. It was believed that a boundary line between the two could be drawn at a value of the basicity ratio somewhere near  $b = 2$ .

**Slags of High Basicity:** The molar composition of slags of higher basicity was calculated by neutralizing 1 mol of acids ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) with 2 mols of bases (CaO, MgO). It was assumed, therefore, that these slags contained the following undissociated compounds:  $2(\text{CaO}, \text{MgO}) \cdot \text{SiO}_2$ ;  $2(\text{CaO}, \text{MgO}) \cdot \text{Al}_2\text{O}_3$ ; CaO; MgO; FeO; CaF<sub>2</sub>. It was further assumed that the mol fractions of free CaO and MgO were in the same ratio as the ratio of their total amounts. The expression *excess* CaO is used to denote the mol fraction of free lime arbitrarily defined by this method of computation in accordance with a concept first introduced by Sherman and Grant.<sup>3</sup>

The sulphur ratio  $\frac{(\%S)}{a_s}$  is plotted in Fig. 1 vs.

mol pct FeO. The points corresponding to a basicity ratio  $b < 2.3$  could not be correlated in this manner; hence Fig. 1 represents only points characterized by a basicity ratio larger than 2.3. It is felt that the spread of the points is mostly imputable to inhomogeneities of these slags, which were the most basic and had a limited fluidity. The spread could not be reduced by a correlation with basicity ratio, excess base, temperature, or other variables. In particular, the (FeO) analysis for the point at  $(\%S)/a_s = 19.3$  is believed to be in excess of the true value. On the same figure the points represented by squares are average values obtained from the data of Grant and Chipman<sup>1</sup> for slags of equal value of "excess CaO" but higher (FeO) content; they fit the selected curves very well.

**Slags of Intermediate Basicity:** Slags included in this group range from 1 to 2.3 basicity ratio (all the leaner basic slags which were not plotted in Fig. 1). Their molar composition was calculated by neutralizing 1 mol of acids ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) with 1 mol of bases (CaO, MgO). It was assumed therefore that these slags contained the following undissociated compounds:  $(\text{CaO}, \text{MgO}) \cdot \text{SiO}_2$ ;  $(\text{CaO}, \text{MgO})$

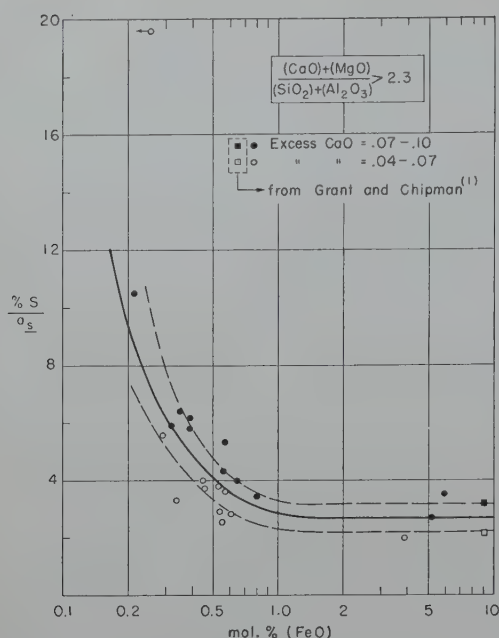


Fig. 1—Effect of iron oxide in the slag upon desulphurization ratio for slags of higher basicity at  $T = 1600^\circ$  to  $1700^\circ\text{C}$ . Neutralization of the acids on 2:1 basis.

$\cdot\text{Al}_2\text{O}_3$ ;  $\text{CaO}$ ;  $\text{MgO}$ ;  $\text{FeO}$ ;  $\text{CaF}_2$ . Again, as for the slags of the preceding group, it was assumed that the mol fractions of free  $\text{CaO}$  and  $\text{MgO}$  were in the same ratio as the ratio of their total amounts. The expression *excess CaO* is used to denote the mol fraction of free lime arbitrarily defined by this method of computation.<sup>8</sup>

The sulphur ratio  $\frac{(\%S)}{a_S}$  is plotted in Fig. 2 vs.

mol pct (FeO). It can be seen that a good correlation is found between sulphur ratio, mol pct (FeO) and *excess CaO*. The point represented by a square and plotted on the same figure is the average value of the sulphur ratio obtained from the data of Grant and Chipman<sup>1</sup> for slags of corresponding basicity but higher (FeO) content.

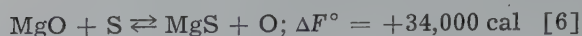
### Discussion of Results

The data plotted in Figs. 1 and 2 cover all the experimental slags available from this investigation, for temperatures ranging from  $1550^\circ$  to  $1700^\circ\text{C}$ . They show that desulphurization is mainly controlled by two factors: Concentration of free lime, and concentration of iron oxide in the slag. The desulphurization ratio is increased by increasing amounts of free lime and by increasing reduction of the slag. The latter factor becomes controlling only at the low (FeO) concentrations, presumably when (FeO) is lower than 2 mol pct.

A more complete interpretation of these results will be obtained by considering the slags of intermediate basicity, which are plotted in Fig. 2. They represent the largest group of slags and therefore appear to be the best testing ground for the assumptions involved.

Magnesia has not been considered as an effective desulphurizer, but as a basic oxide, the effect of which is only to increase the basicity of the slag. A thermodynamic justification can be reached by

comparing the desulphurizing power of basic oxides, according to the reactions:



The equilibrium constants for these reactions have been calculated by Chipman.<sup>18</sup> At  $1600^\circ\text{C}$  they have the following values:

$$K_{\text{CaO}} = \frac{a_{\text{CaS}\cdot\text{O}}}{a_{\text{CaO}\cdot\text{S}}} = 0.04 \quad [7]$$

$$K_{\text{MgO}} = \frac{a_{\text{MgS}\cdot\text{O}}}{a_{\text{MgO}\cdot\text{S}}} = 1 \times 10^{-4} \quad [8]$$

Although exact data on the activities of oxides and sulphides in liquid slags are lacking, it is apparent that lime is about 1000 times a better desulphurizer than magnesia, when the desulphurization is controlled by the above reactions. This conclusion was confirmed by Sherman and Grant,<sup>3</sup> who found no effect of magnesia upon desulphurization in equilibrium blast-furnace slags. In basic open-hearth slags, the sulphur removal is mainly produced by the distribution of iron sulphide between slag and metal.<sup>1</sup> In this latter case the distribution ratio appears to be controlled by the *excess base*, as expressed by Grant and Chipman,<sup>1</sup> and magnesia may play an equal role with lime in increasing the basicity of the slag.

The shape of the curves plotted in Figs. 1 and 2 suggests that in the low (FeO) range desulphurization is controlled predominantly by reaction 3. This would imply the validity of the equilibrium constant  $K$  as expressed by eq 4. Under the simplifying assumptions employed, it is possible to define for each slag-metal couple an equilibrium product:

$$K' = \frac{(\%S) \cdot (\text{mol \% FeO})}{a_S \cdot (\text{excess CaO})} \quad [9]$$

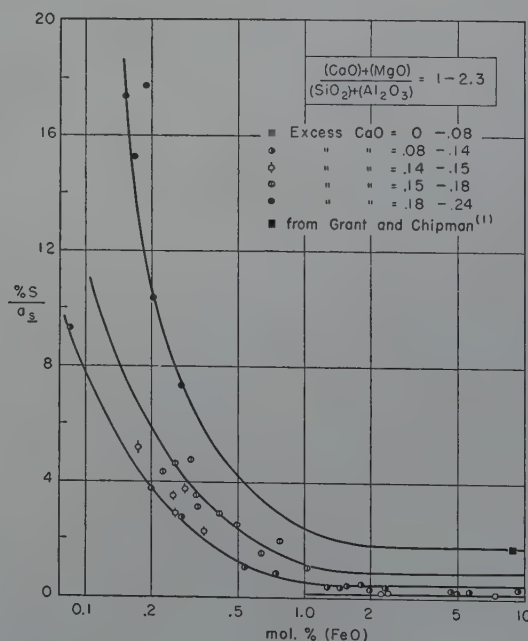


Fig. 2—Effect of iron oxide in the slag upon desulphurization ratio for slags of intermediate basicity at  $T = 1550^\circ$  to  $1700^\circ\text{C}$ . Neutralization of acids on 1:1 basis.



Taking into account the prevailing sources of errors in the present investigation, the average value of  $K'$

can be best obtained from a plot of  $\frac{(\%S)}{a_s} \cdot (\text{mol } \%$

FeO) vs. (excess CaO). This plot is shown in Fig. 3. The points plotted represent all the slags of intermediate basicity ( $1 < b < 2.3$ ) which are also plotted in Fig. 2, with the exclusion of slags analyzing more than 2.3 mol pct FeO. The temperature range is 1550° to 1700°C. A differentiation of the points on the basis of temperature had shown, however, no significant trend; hence the effect of temperature is assumed to be small.

If  $K'$  were constant, the points would define a straight line, passing through the origin of the coordinates and with a slope equal to  $K'$ . It is clear, however, that the points plotted define a curve and a variable value of  $K'$ . This can be expected since the range of basicity covered is very large and varies from  $b = 1$  to  $b = 2.3$ . The plot of Fig. 3 shows that the points characterized by a basicity value ( $b$ ) above 1.9 diverged most from the ideal straight line, especially at the higher values of excess CaO. Such behavior can be accepted as evidence that the actual constitution of the liquid slag is not that indicated by the arbitrary formulas assumed in the present method of calculation.

A computation of the activities of slag constituents in a pure binary CaO-SiO<sub>2</sub> slag was carried out by Murray and White<sup>14</sup> on the basis of assumptions probably more accurate than those employed in the present calculations. Their values would show that near the orthosilicate composition the activity of "free CaO" increases more rapidly than the "excess CaO." This would justify, at least qualitatively, a deviation similar to that verified in Fig. 3.

The equilibrium blast-furnace slags studied by Hatch and Chipman<sup>2</sup> fall into the basicity range  $1 < b < 1.9$ , and they can be plotted in Fig. 3. For this plot, the value of excess CaO has been calculated in the same manner as for all other slags plotted in Fig. 3, namely on the basis of a 1:1 saturation of the bases. The points chosen are those taken at 1500°C and averaging 1.55 pct S in the slag. Sherman and Grant<sup>8</sup> have shown already that the ratio  $(\%S)/S$  was, for these slags, directly proportional to the (excess CaO). The value of the activity of sulphur in pig iron,  $a_{S_i}$ , is calculated by the use of the activity coefficient in the presence of carbon<sup>15</sup>  $f_{S_c}^S$  and in the presence of silicon<sup>11</sup>  $f_{S_{Si}}^S$ . It is assumed that, in the presence of both carbon and silicon, the resulting activity coefficient is the product of the two separate values:<sup>14</sup>

$$f_{C, Si}^S = f_{C_c}^S \cdot f_{S_{Si}}^S$$

An average activity coefficient of 5.7 is obtained, and the resulting ratio  $(\%S)/a_s$  yields values from 20 to 60 as compared with  $(\%S)/S = 100$  to 400. The blast-furnace slags<sup>2</sup> were analyzed again for FeO and averaged 0.027 to 0.030 wt pct (FeO); this corresponds to an average value of 0.040 for

the mol pct (FeO). The plot of  $\frac{(\%S)}{a_s} \cdot (\text{mol } \%$

FeO) vs. excess CaO for these slags is shown in Fig. 3 by the use of black squares. The points fit a

straight line, which can be extrapolated to the origin, and which also fits the points obtained in this investigation for  $1 < b < 1.9$ .

The agreement between blast-furnace slags and highly reducing slags of the electric-furnace range shows that in both cases desulphurization is controlled by eq 3. The value of the equilibrium product  $K'$  is obtained directly from the slope of the straight line in Fig. 3:

$$K' = 6.5 \quad \text{for } 1 < b < 1.9$$

$$\text{and } 0.040 < (\text{mol } \% \text{ FeO}) < 2.0 \quad [9a]$$

It also follows that the data obtained in the present investigation can be extrapolated to the blast-furnace range. This is shown by Fig. 4 in which the squares represent average values for blast-furnace slags at several excess CaO levels. The remaining points are plotted from Fig. 2. The plot is on a log-log basis, and the straight portion of the lines has an inclination of 45° in agreement with the approximate constancy of  $K'$ . The dashed line in Fig. 4 does not fit the blast-furnace data, although the value of excess CaO is the same for both. This is to be expected, since the blast-furnace slags under consideration all have  $b < 1.9$  and thus show a constant value of  $K'$ , while the points represented by the dashed line all have higher basicity and are those which deviate from the straight line in Fig. 3.

It is now possible to draw a comprehensive picture of desulphurization in all ranges of (FeO) concentration. Based on the molecular theory, desulphurization is controlled by the following reactions:



Under highly reducing conditions, as in the blast furnace, reaction 2 is pushed far to the right, and all or most of the sulphur in the slag is in the form of CaS. Pure partition of FeS plays a minor role, and, for all purposes of calculation, the sulphur in the slag in the form of (FeS) can be neglected.

In open-hearth and electric-furnace slags sulphur may be present both in the form of (FeS) and

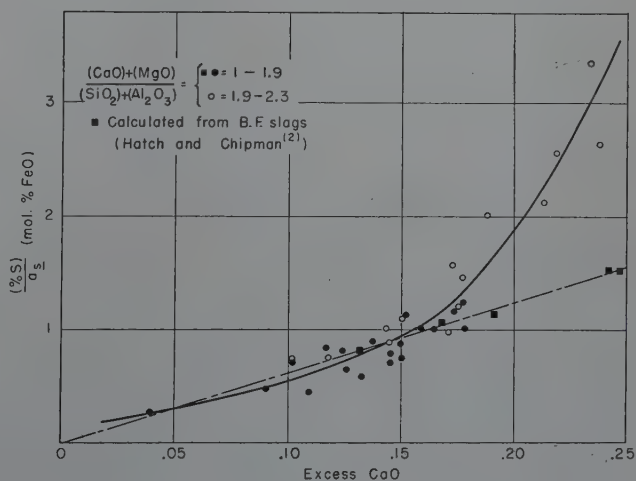


Fig. 3—Influence of basicity on the equilibrium product  $K'$ . Neutralization of the acids on 1:1 basis.

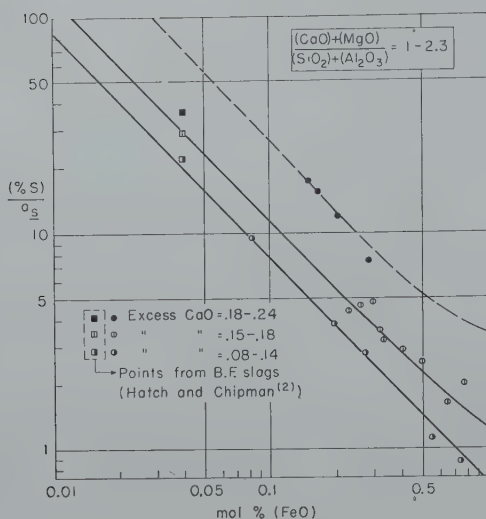


Fig. 4—Extrapolation of the data for slags of intermediate basicity to the range of blast-furnace slags. Neutralization of the acids on 1:1 basis.

(CaS). The total desulphurization ratio then is given by the equation:

$$\frac{(\%S)}{a_s} = \frac{(\%S_{Fe}) + (\%S_{Ca})}{a_s} \quad [10]$$

and one may write, similarly to Bardenheuer and Geller<sup>4</sup> and Wentrup:<sup>16</sup>

$$\frac{(\%S)}{a_s} = L_{FeS} + K'' \cdot \frac{a_{CaO}}{a_{FeO}} \quad [11]$$

where:

$$L_{FeS} = \frac{(\%S_{Fe})}{a_s} \quad [12]$$

and:

$$K'' = \frac{(\%S_{Ca})}{a_s} \cdot \frac{a_{FeO}}{a_{CaO}} \quad [13]$$

The value of  $L_{FeS}$  depends on the composition of the slag, and it is difficult to evaluate it when part of the sulphur in the slag is in the form of  $(S_{Ca})$ . The only value known for  $L_{FeS}$  is that in pure iron oxide slag ( $L_{FeS} = 3.6$  at  $1600^\circ\text{C}$ ). For slags more basic than the orthosilicate composition, in the approximate range from 10 to 30 pct (FeO) the total desulphurization ratio appears to be independent of (FeO) concentration and excess base is the main

controlling factor.<sup>1</sup> A probable explanation of this result may be found in the high value of  $L_{FeS}$  for these slags: In particular, at high (FeO) concentrations,  $(S_{Ca})$  is only a fraction of the total sulphur in the slag, and  $(\%S)/a_s$  practically coincides with  $L_{FeS}$ . Furthermore,  $L_{FeS}$  is of the same order of magnitude as the partition coefficient for pure iron-oxide slag, so that additions of (FeO) do not affect it too significantly.

This is not the case for less basic slags like the slags of intermediate basicity which form the bulk of this investigation. The partition coefficient  $L_{FeS}$  is lowered with decreasing basicity of the slag, and the values of  $(S_{Ca})$  cannot be neglected as soon as they become of the same order of magnitude as  $(S_{Fe})$ . The influence of (FeO) on these slags cannot be merely that of a diluent, for high (FeO) concentrations, since the partition coefficient for pure iron-oxide slag may be many times higher than that of the original slag. Hence, addition of FeO to slags of intermediate basicity must increase their partition coefficient. The plot of desulphurization ratio in the ternary diagram FeO — (CaO + MgO) —  $\text{SiO}_2$ , as given by Fetter and Chipman,<sup>8</sup> also shows a similar trend. Experimental data on the variation of  $L_{FeS}$  with (FeO) concentration, for a slag of given basicity, are lacking however, and some simplifying assumptions are necessary. On the basis of the work of Bardenheuer and Geller,<sup>4</sup> one may consider  $L_{FeS}$  to vary linearly in the whole (FeO) range. It is then necessary only to estimate the value  $L_{FeS}^\circ$  that  $L_{FeS}$  will assume for (FeO) = 0, since it is known that  $L_{FeS} = 3.6$  when (FeO) = 100 pct (at  $1600^\circ\text{C}$ ). In the present case, values of  $L_{FeS}^\circ$  were assumed which would fit the points for the two lower lines in Fig. 4. Accordingly, it was determined at (FeO) = 0:

$$\begin{aligned} b = 1.7 & \quad L_{FeS}^\circ = 0.3 \\ b = 1.5 & \quad L_{FeS}^\circ = 0.1 \end{aligned}$$

The values reported for the basicity  $b$  correspond to an excess CaO (on 1:1 basis) = 0.15 and 0.10, respectively, for the high magnesia slags under consideration.

On the basis of the chosen values of  $L_{FeS}^\circ$  and of the linearity assumed for  $L_{FeS}$  in the range 0 to 100

pct (FeO), the values of  $\frac{(\%S_{Fe})}{a_s}$  are given directly in Fig. 5 as a function of mol pct (FeO).

It is now possible to solve eq 11 which, on the basis of the molecular assumptions employed, can be written as follows:

$$\frac{(\%S)}{a_s} = L_{FeS} + K' \frac{(\text{excess CaO})}{(\text{mol \% FeO})} \quad [11a]$$

The solution of this equation is shown in Fig. 6.

The values of  $L_{FeS} = \frac{(\%S_{Fe})}{a_s}$  are obtained from

Fig. 5 and are represented by the dashed lines which end at the point at  $\frac{(\%S)}{a_s} = 3.6$ , and (FeO) = 100

pct. The values of  $\frac{(\%S_{Ca})}{a_s} = K' \frac{(\text{excess CaO})}{(\text{mol \% FeO})}$

are expressed by the straight lines inclined at  $45^\circ$

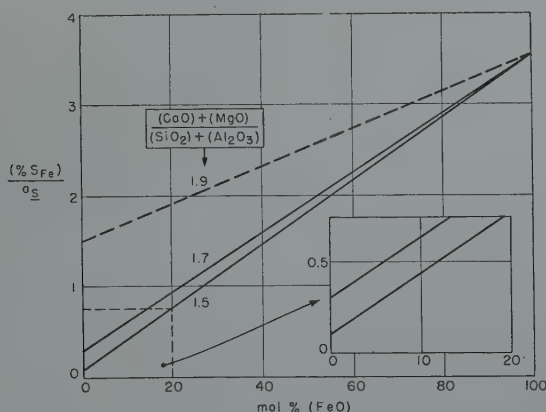
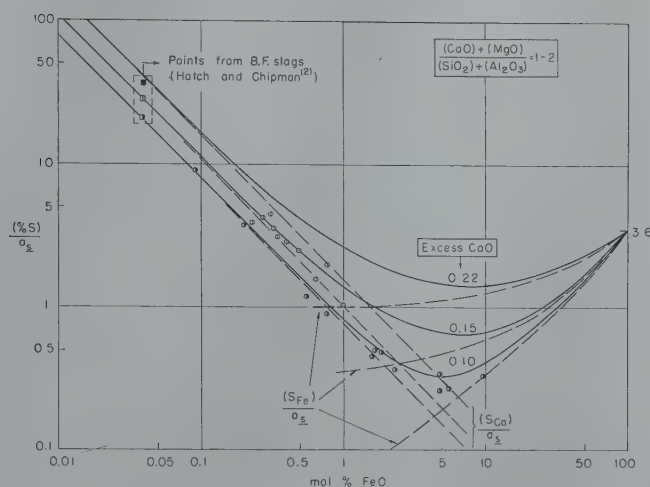


Fig. 5—Assumed influence of (FeO) on the distribution coefficient of iron sulphide.



Fig. 6—Distribution of total sulphur as a function of iron oxide in the slag. Neutralization of the acids on 1:1 basis.



and represent an extrapolation from Fig. 4. The full lines in this diagram give the solution of eq 11a and have been obtained by addition of the corre-

sponding values of  $\frac{(\%S_{Fe})}{a_s}$  and  $\frac{(\%S_{Ca})}{a_s}$ . While

the lines traced for excess CaO = 0.10 and 0.15 stem from the application of definite assumptions, the line for excess CaO = 0.22 is purely hypothetical. All lines have been carried through to (FeO)

= 100 pct to show their common point at  $\frac{(\%S)}{a_s} =$

3.6; although the value of excess CaO vanishes as (% FeO) approaches 100 pct. The experimental points from the pertinent ranges of (excess CaO) are also plotted in Fig. 6. The fact that these points seem to substantiate the theoretical curves should not be taken as a proof of the correctness of the assumptions employed. The diagram is traced on a log-log basis and is greatly expanded in the range of the lower desulphurization ratios. In this range, other curves, which apparently would not be fitted by the points, might still be in good agreement with them, if plotted on a conventional scale. Thus values double those assumed for  $L_{FeS}^\circ$  could still be considered to fit the experimental data, although they would appear to disagree with them, on the basis of the plot of Fig. 6. The full lines in Fig. 6 show that the mechanism of desulphurization, in the full range of (FeO) concentrations, can be explained by the reaction 3.

It is further shown that the constancy of the desulphurizing ratio in a large range of (FeO) concentration does not imply a mere partition of FeS between slag and metal but is also verified on the hypothesis of the overall reaction 3. When the basicity is sufficiently high, the constancy of the desulphurization ratio is extended to a large range of (FeO) concentration. In this range, from the standpoint of calculations, it is indifferent whether desulphurization is carried out by a mechanism of pure partition, as expressed in eq 1, or by a reaction, as expressed in eq 3. This is shown in Fig. 7, in which the range of slags of basicity higher than 2 has been sketched in its estimated position. The slags investigated by Grant and Chipman<sup>1</sup> are outlined by the heavy lines, and it appears clearly that, for these slags, (FeO) has little effect on their desulphurizing power over a large range of iron oxide

concentration in the slag. Fig. 7 also illustrates how the different fields of steelmaking are connected by the desulphurization reaction. In the blast furnace, partition of FeS plays a minor role: In the open hearth it plays the main role. Finally, the reducing slags of the electric furnace represent the transition between the two prevailing mechanisms.

The previous discussion has been based on the assumption that molten slags are composed of molecular compounds and their constituent oxides. However, as already pointed out by Hatch and Chipman for blast-furnace slags,<sup>2</sup> this does not imply that the actual structure of molten slags is similar to that assumed in this discussion. On the contrary, it is more probable that the real structure of a slag is intermediate between an ideal ionic solution and a mixture of partially dissociated compounds. From the standpoint of calculations this would be equivalent to assuming a more complete dissociation of the compounds in the slag. The expression of equilibrium in terms of atoms or groups of atoms, instead of definite compounds, might lead to a more accurate evaluation of the experimental results, but in the actual state of investigations the pertinent data lack the necessary accuracy and still would need some more or less arbitrary assumptions. This is particularly true for the slag systems studied in the present investigations, which are high in silica and magnesia concentrations, and thus require the assumption of the formation of

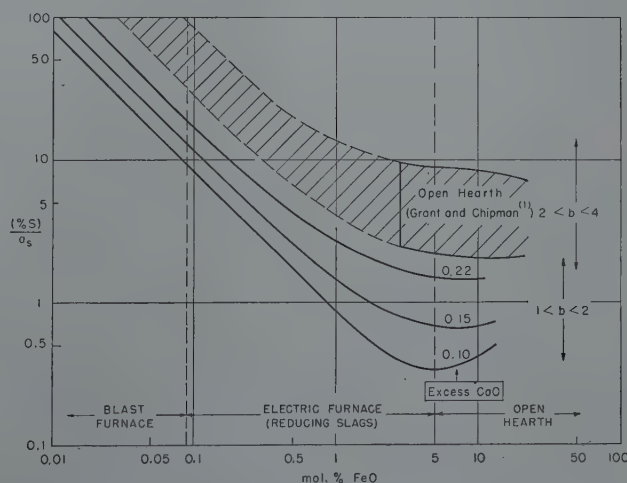
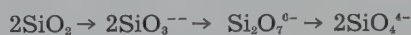


Fig. 7—Desulphurizing power of basic steelmaking slags. Neutralization of the acids on 1:1 basis.

complex ions. For such a case simpler assumptions, similar to those employed in this investigation, seem to yield values of the activities of the different components which are probably proportional to the true values, in definite ranges of composition. It is clear however that their absolute values may not be comparable with the true values, outside of the criterion of limited proportionality outlined above.

Even if quantitative calculations appear problematical, the concept of ionization is useful for a qualitative analysis of the results. In the transition from acidic to basic solutions the silicate ions probably follow a series of steps:



and each step requires the addition of oxygen ions. Thus the number of relatively free oxygen ions does not increase proportionally with the addition of metal oxides to a silicate slag. Also a limited desulphurizing power of magnesia, compared to lime, can be expected, since the binding forces between magnesium and oxygen ions are greater than those between calcium and oxygen ions.<sup>17</sup> Hence,<sup>2</sup> the substitution of 1 mol of magnesia for 1 mol of lime in a slag would result in a decrease in the oxygen-ion concentration.

### Summary and Conclusions

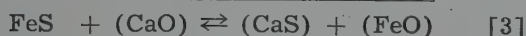
This investigation has studied the influence of basicity and (FeO) content of the slag upon sulphur distribution between molten iron and slags of low (FeO) concentration. These slags are similar to those encountered in the electric furnace during the reducing stage. It has been possible to extrapolate the data obtained to the blast-furnace and to the open-hearth range, and the following conclusions have been reached.

1—Satisfactory correlations are found by computing the molar composition of the slags on the basis of a complete neutralization of the acids ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ). Such a neutralization is assumed to require 2 mols of bases (CaO, MgO) per mol of acid for the more basic slags, and 1 mol of bases per mol of acids for the less basic slags. The boundary between the two methods of computation is found in a range

near the value of the basicity  $b = \frac{N_{\text{bases}}}{N_{\text{acids}}} = 2$ , and

in this range neither method of computation is entirely satisfactory.

2—Influence of FeO: For all FeO concentrations desulphurization can be explained on the basis of the following reactions:



$$K = \frac{a_{\text{FeO}} \cdot a_{\text{CaS}}}{a_{\text{CaO}} \cdot a_{\text{S}}} \quad [4]$$

In highly reduced slags [(FeO) < 2 pct] desulphurization is mainly controlled by reaction 2 and the desulphurization ratio increases rapidly with decreasing (FeO) content of the slag.

In slags containing higher amounts of (FeO) reaction 1 gradually acquires importance since the amount of sulphur combined with lime decreases rapidly as (FeO) increases. Finally, for higher

amounts of (FeO) in the slag (FeO > 10 pct), the sulphur combined with lime becomes a small fraction of total sulphur present in the slag, and reaction 1 is the predominant controlling factor. The desulphurization ratio, in this range, is approximately independent of the (FeO) concentration for slags of the basic open-hearth type.

3—Influence of CaO: For all slags containing less than 10 pct FeO the value of excess CaO computed by the method of Sherman and Grant<sup>8</sup> is also one controlling factor, and the desulphurization ratio increases with increasing amounts of excess CaO. Magnesia has little or no desulphurizing power in this range, its only effect being that of increasing the basicity of the slag.

### Acknowledgment

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# Vacuum Treatment of Parkes' Process Crusts On a Pilot-Plant Scale

by A. W. Schlechten and R. F. Doelling

**Parkes' process crusts were vacuum distilled using a shortened Pidgeon retort. Zinc was effectively removed below 800°C and recovered as a zinc sheet easily stripped from the furnace liner. Lead distillation required about 950°C and the resulting lead condensate tended to stick to the thin metal liner. Final purity of residue is limited only by nonvolatile metals such as copper.**

THE successful commercial application of vacuum distillation for the removal of zinc from lead, as described by W. T. Isbell,<sup>1</sup> raises the question of whether or not a similar method can be used for other metal separations. Preliminary laboratory experiments on the vacuum distillation of Parkes' crusts by one of the authors<sup>2</sup> gave such encouraging results that it was decided to make a series of tests with large scale equipment to determine the results that might be expected in plant operation. The pilot-plant test results are reported in this paper.

The great advantages of vacuum dezincing are its simplicity, the relatively low temperature of operation, and the fact that the zinc is recovered in the metallic state ready for use again in the desilverization of lead bullion. These same advantages and others would be realized from the vacuum distillation of the zinc-lead-silver crusts made in the Parkes' process. Zinc readily will distill over at temperatures of 800° to 900°C as contrasted with the 1200°C or more used in the Faber du Faur furnace. Furthermore, the recovery of zinc as metal is practically perfect since there is no loss by oxidation or fuming.

If the vacuum distillation is continued and hastened by raising the temperature to around 1000°C, the lead will distill over at an appreciable rate and deposit in a warmer zone of the condenser. This lead will contain a small amount of silver, but it can be returned to the desilverizing kettles and there is not the chance of loss that there is in disposing of the rich litharge from cupelling. The lower temperatures required will mean a saving of fuel and less wear on the equipment. One further point is that the vacuum distillation could be run

on a small scale practically continuously, so as to avoid the accumulation of large amounts of silver-rich material and the need of assembling a large crew for special cupellation runs.

It should be pointed out here that the final purity of the silver residue will depend on the copper or iron content of the crusts, as these and other metals with low vapor pressure will not be eliminated.

The idea of treating the silver-zinc-lead crusts from the desilverization of lead bullion by vacuum distillation is not a new one, but such experiments have not been reported, as far as can be determined. In 1912, T. Turner presented a paper<sup>3</sup> before the Institute of Metals on the vacuum distillation of brass, and a member of the audience suggested that he try his method on Parkes' crusts. In 1935, W. J. Kroll, noted for his discovery of debismuthizing lead by calcium additions, published a paper<sup>4</sup> on vacuum distillation of metals and pointed out possible applications in the lead industry.

## Principles of Separation

The successful separation of two or more metals by distillation depends upon an appreciable difference in the effective vapor pressures of the metals in the alloy to be treated. The vapor pressures of the common metals have been determined with considerable accuracy; for example, at 800°C the vapor pressures of the individual metals which are of particular interest in this paper are about as follows: Zn, 241 mm; Pb, 0.0553 mm; and Ag, 0.000276 mm.

Unfortunately, data are not available on the activities of the components in the ternary system Zn-Pb-Ag, but it can be estimated that on the basis of the vapor pressures of the individual metals a good separation can be made by distillation. The preliminary laboratory tests previously mentioned<sup>2</sup> supported this assumption.

The pilot-plant size vacuum distilling furnace is shown in Fig. 1. It consisted of an abbreviated Pidgeon retort, 5 ft long with an ID of 8 in., heated by six silicon carbide elements placed symmetrically

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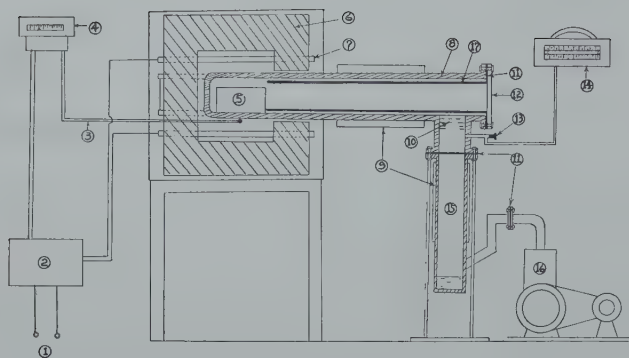


Fig. 1—Vacuum retort.

- |                        |                          |
|------------------------|--------------------------|
| 1—Power supply         | 9—Water jackets          |
| 2—Magnetic switch      | 10—Baffle                |
| 3—Thermocouple         | 11—Gaskets               |
| 4—Pyrometer controller | 12—Retort cover          |
| 5—Boat                 | 13—Valve to break vacuum |
| 6—Furnace insulation   | 14—McLeod gage           |
| 7—Glo-bar elements     | 15—Diffusion pump        |
| 8—Retort               | 16—Mechanical pump       |
|                        | 17—Retort liner          |

around and parallel to the retort. The temperature was measured by a chromel-alumel thermocouple peened to the outside of the retort under the charge.

The retort was connected directly to a 6-in. oil diffusion pump, Type 104, manufactured by the National Research Corp. The diffusion pump, in turn, was connected to single-stage mechanical vacuum pump, Type VSD 778, made by the Kinney Manufacturing Co. The details of temperature control and vacuum measurement can be seen from the figure. A boat to hold the charge was made of 1/16-in. sheet iron, and a 20-gage black iron sheet was inserted in the cold end of retort to serve as a liner on which the metal vapors could condense. A simple baffle in the connection between the retort and the diffusion pump effectively prevented the zinc vapors from entering the pump.

### Experimental Procedure

The experimental work was conducted to determine, first, the effect of time, temperature, pressure, and amount of charge on the quality of products obtained, and to determine, second, whether the operation could be carried out practically without too many difficulties.

In a typical run, the mechanical pump brought the pressure in the system down to 100 microns within 5 to 10 min at which time the diffusion pump was turned on. In an additional 20 min the diffusion pump reduced the pressure to the 10 to 30 micron range where most of the runs were made. The evacuation of the retort was accomplished so rapidly that the heating could be started at the same time as the pumps without fear of oxidizing the charge.

When the desired furnace temperature was reached, little attention was needed except for an occasional check on the pressure and the cooling jacket water. At the end of the heating cycle the furnace was turned off and the retort was allowed

to cool to about 200°C, then the pumps were stopped, and the retort was opened. In order to more nearly duplicate expected plant procedure, the above operations were hastened in Runs 20 and 21 by charging and discharging the retort when it was almost at operating temperature.

### Materials, Sampling, and Analytical Methods

The crusts used for experimentation were obtained from two different lead smelters; the composition of the crusts given in Table I are the mean of numerous analyses made on several samples. Crust No. 1 was a typical pressed crust although somewhat high in copper. Crust No. 2 was a liquated crust and was low in lead; the appreciable amount of iron was probably picked up from the liquating kettle.

The products of the furnace consisted of a condensate and a residue. The condensate could be roughly divided into a sheet, mainly zinc, which stripped easily from the liner and a high lead material from the hot end of the liner. The high lead material, which had condensed in the liquid state, consisted of small droplets and of larger masses which had run together and solidified.

The condition of the residue depended on the operating temperature. After runs of 800°C or less the residue was granular and broke up easily. If the temperature went above 800°C, partial fusion or even complete melting took place and the residue was in one solid piece.

### Experimental Results

The results of the various runs showed the effect of time, temperature, pressure, and size of charge on the completeness of distillation and the final composition of the residue. These results can be shown best graphically by grouping the data from a series of runs with but one variable.

*Effect of Time:* Figs. 2 and 3 show respectively the weight of the various metals in the residue after runs of varying time on Crust No. 1, the high lead crust, and Crust No. 2, the liquated crust; the tem-

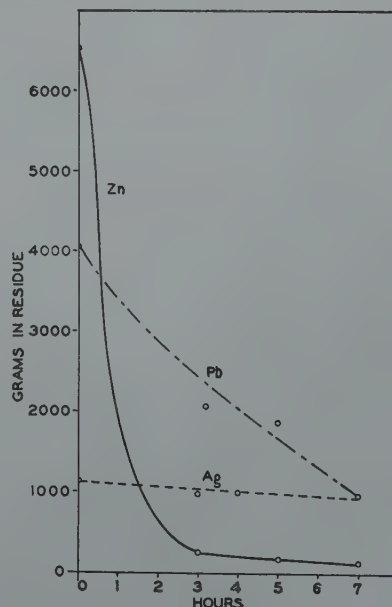


Fig. 2—Weight of metals in residue from distillation of Crust No. 1 for various lengths of time.

Charge, 12,000 g; temperature, 900°C; pressure, 17 to 40 microns.

Table I. Composition of Crusts

| Number      | Zn, Pct | Pb, Pct | Ag, Pct | Fe, Pct | Cu, Pct | Total |
|-------------|---------|---------|---------|---------|---------|-------|
| Crust No. 1 | 54.45   | 33.79   | 9.45    | 0.70    | 2.00    | 99.69 |
| Crust No. 2 | 63.70   | 8.60    | 26.85   |         |         | 99.85 |



perature was the same and the pressure essentially the same for each group. Both graphs show the same pattern of the early and rapid elimination of practically all of the zinc accompanied by a slower, but steady, elimination of lead, and a very gradual loss of silver from the residue.

**Effect of Temperature:** Fig. 4 shows the weight of the various metals left in the residue of Crust No. 2 when the temperature is increased; the time and the amount of charge were the same and the pressure essentially the same in each run. The graph shows that the zinc is removed effectively at the lowest temperature used, but that the higher temperatures are needed for the removal of the lead if a time of 3 hr is used.

**Effect of Charging Hot Retort:** The time of the runs reported in the previous sections refer to the time at operating temperature; the time to bring the retort to temperature and to cool it was not included. This raises two questions: First, how much of the effective distillation takes place in the heating and cooling times, and second, can the retort be charged and discharged while hot without detrimental oxidation of the charge or the products? To settle these points, two runs were made in which the retort was charged at 800°C, sealed and pumped down, brought to 900°C, held for 3 hr, cooled to 850°C, and then opened. The products were removed immediately; the overall time was about 4 hr.

As can be seen from Fig. 5, the results are much the same as with the longer procedure. Only on the weight of lead left in the residue can it be seen that the distillation during the heating and cooling periods helps eliminate a slight amount more of metal. The elimination of zinc is so nearly complete in all instances that no difference can be detected, and the distillation of silver is so slight that no difference can be seen.

Certainly the hot charging had no detrimental effect that can be noticed and accomplished almost as much as the runs with the long heating and cooling periods.

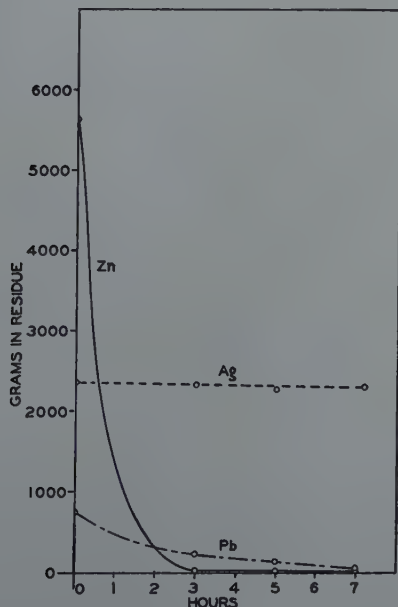


Fig. 3—Weight of metals in residue from distillation of Crust No. 2 for various lengths of time.

Charge, 8854 g; temperature, 950°C; pressure, 17 to 32 microns.

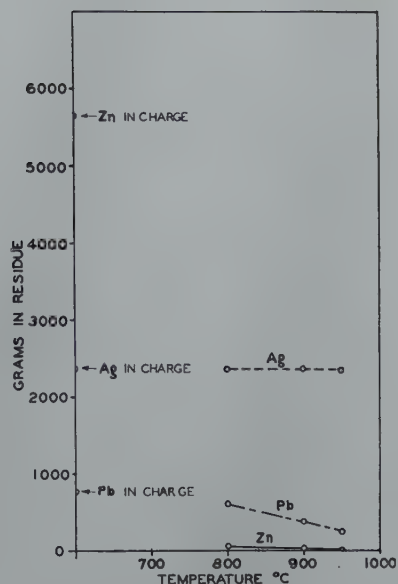


Fig. 4—Weight of metals in residue from distillation of Crust No. 2 at various temperatures.

Charge, 8854 g; time, 3 hr; vacuum, 28 to 50 microns.

**Effect of Pressure:** The rate of distillation of all of the metals should be greater at lower residual pressures in the retort. The question arises as to whether the slightly greater rate of distillation warrants the use of pressures as low as 10 to 30 microns. These lower ranges almost require a diffusion pump in the circuit, if any speed of pumping is desired.

Several runs were made using only the mechanical pump so that pressures of 120 to 135 microns were measured. The results of these runs also are shown in Fig. 5 and again any difference is only apparent in the lead content. The amount of lead eliminated after 3 hr at 900°C is not quite as great at the higher pressures. However, this difference is so slight that a small increase in the time or temperature would overcome it. It would appear that there is no real advantage in using pressures less than 100 or 150 microns.

**Effect of Size of Charge:** The retort used for these experiments was only 5 ft long as compared with the 10 ft retorts used at some commercial magnesium plants. These commercial retorts could take a much larger charge, so it was desirable to know how the size of charge would affect the distillation. The results are shown in Table II.

Apparently the zinc is evaporated for the most part in the heating period before the charge becomes molten. Since in the solid state the surface area is a function of amount of charge, about the same

Table II. Distillation of Crust No. 1, 900°C, 3 Hr, 17 to 40 Microns

| Zn        |            |                       |                         | Pb         |                       |                         |
|-----------|------------|-----------------------|-------------------------|------------|-----------------------|-------------------------|
| Charge, G | Charged, G | Evap-<br>orated,<br>G | Evap-<br>orated,<br>Pct | Charged, G | Evap-<br>orated,<br>G | Evap-<br>orated,<br>Pct |
| 3,555     | 1936       | 1936                  | 100.0                   | 1201       | 1183                  | 98.5                    |
| 8,858     | 4823       | 4701                  | 97.8                    | 2993       | 2105                  | 70.9                    |
| 12,000    | 6734       | 6494                  | 96.3                    | 4055       | 1978                  | 48.6                    |
| 18,028    | 9810       | 9481                  | 96.6                    | 6092       | 1946                  | 32.0                    |

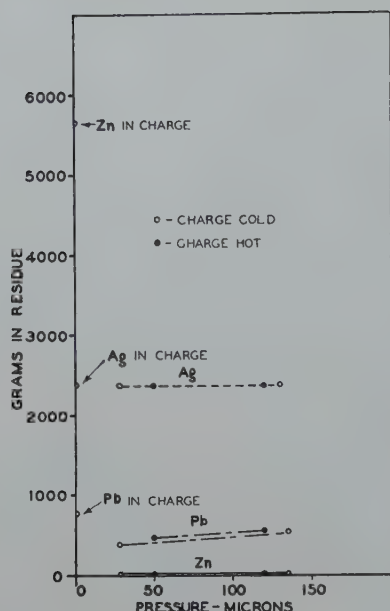


Fig. 5 (left)—Weight of metals in residue after distillation of Crust No. 2 at different pressures and with different conditions of charging and discharging.

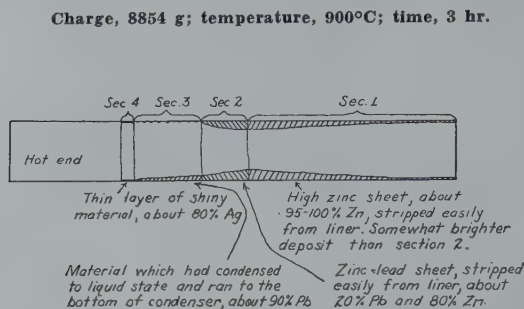


Fig. 6—Distribution of metal in condensate.

degree of zinc removal is obtained. The major portion of the lead, however, is evaporated after the temperature is above the melting point of the crust, and in this case the surface area is independent of amount of charge except with respect to the cross-section of the boat at various depths. The boat which was used apparently had a cross-section such that at the operating conditions about 2000 g of Pb could be evaporated in 3 hr. From these data then the optimum charge for the given conditions and the boat being used can be calculated.

**Loss of Silver to Condensate:** With the extended time and higher temperatures necessary for the distillation of lead, some silver will also be carried over into the condensate. This carry-over is not a true loss as the silver will be largely in the condensed zinc and lead which can be returned to the desilverizing kettles.

The distribution of the silver in the various products is shown in Fig. 6 and in Table III which records the results of a run in which both the lead and zinc were removed almost completely. The final purity of the residue was kept down by the excessive amount of copper in the original crusts. It can be

Table III. Distillation of Crust No. 1, 1000°C, 3 Hr, 21 Microns

|                     | Wt, G | Pb, Pct | Re-cov-ery Pb, Pct | Zn, Pct | Re-cov-ery Zn, Pct | Ag, Pct | Re-cov-ery Ag, Pct | Cu, Pct | Re-cov-ery Cu, Pct |
|---------------------|-------|---------|--------------------|---------|--------------------|---------|--------------------|---------|--------------------|
| Charge Sheet        | 8851  | 33.79   | 100.0              | 54.45   | 100.0              | 9.45    | 100.0              | 2.00    | 100.0              |
| Condensate Granular | 6154  | 19.14   | 39.4               | 78.77   | 100.6              | 0.34    | 2.9                | 0.05    | 1.8                |
| Condensate Residue  | 1705  | 88.18   | 50.3               | 8.25    | 2.9                | 2.29    | 4.7                | 0.21    | 2.0                |
| Unaccounted         | 902   | 0.56    | 0.2                | 0.00    | 0.0                | 74.23   | 80.1               | 18.64   | 95.0               |
|                     | 90    |         | 10.2               |         |                    |         | 12.8               |         | 1.2                |

Table IV. Distillation of Crust No. 2, 950°C, 7 Hr, 17 Microns

|         | Wt, G | Pb, Pct | Re-cov-ery Pb, Pct | Zn, Pct | Re-cov-ery Zn, Pct | Ag, Pct | Re-cov-ery Ag, Pct | Fe, Pct | Re-cov-ery Fe, Pct |
|---------|-------|---------|--------------------|---------|--------------------|---------|--------------------|---------|--------------------|
| Charge  | 8854  | 8.60    | 100.0              | 63.70   | 100.0              | 26.85   | 100.0              | 0.70    | 100.0              |
| Residue | 2407  | 1.74    | 5.5                | 0.23    | 0.1                | 95.65   | 96.9               | 2.38    | 92.4               |

seen that the high-zinc sheet condensate contains about 3 pct of the total silver, while the high-lead granular products contain 4.7 pct of the total silver. The 12.8 pct Ag not accounted for in the analyses condensed in the hottest portion of the condenser as an alloy running about 80 pct Ag. For a single run there was not enough of this material to be recovered, but in practice this would build up to the extent that it could be recovered and ultimately there would be no loss.

The results given in Table III are from the treatment of a low grade crust; much more favorable results can be obtained with a liquated crust as shown in Table IV.

**Operating Conditions:** No difficulty was experienced in maintaining an adequate vacuum in the system or in operating the pumps or furnace. Charging the retort is simple, and the only problem lies in the removal of the products. As mentioned before, the high zinc sheet is easily stripped from the liner, but the high lead material tends to stick. In practice there would be no necessity of complete removal of the condensate and so the sticking would not be too serious.

The residue containing copper tends to stick in the charge boat and will attack a sheet iron boat in runs at a high temperature. It might be preferable, therefore, to make the boat of cast iron or of a ceramic material.

## Conclusions

- 1—Zinc is readily removed from Parkes' process crusts at low temperatures by vacuum distillation.
- 2—Lead can be removed by extended time and increased temperature.
- 3—The purity of the residue will depend upon the amount of nonvolatile metals in the residue. A liquated crust was distilled to yield a residue analyzing 95.7 pct Ag, 2.4 pct Fe, 1.7 pct Pb, and 0.2 pct Zn. This residue contained 96.9 pct of the silver in the charge.

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# Constitution Of Iron-Chromium-Molybdenum Alloys At 1200°F

by Spencer R. Baen and Pol Duwez

**A**LTHOUGH the practical importance of Fe-Cr-Mo alloys has long been recognized, constitution studies have been limited to a few alloys within rather narrow ranges of composition. The purpose of the present study was to establish the phase boundaries in the ternary diagram at a temperature of 1200°F (650°C).\*

The identification of phases and the determination of phase boundaries were based primarily on X-ray diffraction measurements and occasionally on microscopic observation. The methods used for locating the phase boundaries were essentially those described in detail by Andersen and Jette,<sup>1</sup> and by others.<sup>2,3</sup> The compositions of 180 alloys, prepared by powder metallurgy techniques, are shown in Fig. 1. The chemical analysis and mesh size of the powders which were used for the preparation of the alloys are given in Table I.

The powders were mixed for 48 hr or longer, then compacted under 80,000 psi in a ½-in. diam steel die. Each specimen weighed approximately 5 g. The compacts were sintered for 4 hr at 2500°F (1371°C) in an atmosphere of pure dry hydrogen (dew point near the temperature of liquid nitrogen). An open tray of chromium powder was placed upstream of the compacts to act as a "getter" for the last traces of oxygen or water vapor. In many cases this chromium powder was bright after sintering. Occasionally the upstream side of the powder was slightly greenish, but in all cases the downstream side was metallic. Some of the alloys contracted during sintering and some expanded as much as 20 pct. The latter alloys, which in all cases were brittle, were crushed in a tool steel mortar, repressed, and resintered for 4 hr at 2500°F. After sintering, the alloys were aged for ten days at 1200°F (650°C) in evacuated (10<sup>-5</sup> mm Hg or better) fused silica tubes and were cooled rapidly to room temperature following the aging treatment.

\* After this study was completed, a paper on the same subject was published by Putman, Potter, and Grant.<sup>13</sup> These authors investigated the phase boundaries in the Fe-Cr-Mo ternary system at 900°, 1100°, and 1300°C. Duplication of effort was fortunately avoided and the combination of the two studies provides a good picture of the phase relationships in the ternary system at four temperature levels.

The use of the powder metallurgy technique in preparing alloys for structural investigation offers a simple method of avoiding contamination or non-homogeneity which could result from a melting operation. It is very often possible to dispense with chemical analysis of the alloys which have been prepared by the powder metallurgy method. In lieu of chemical analysis, it is necessary to determine the weight of the compact before and after sintering. The chemical composition of the alloy may be considered as that of the green compact, within the limits of accuracy determined by the loss of weight during sintering.

In phase-diagram studies it is important to achieve homogeneity in structure, whether the alloys are prepared by powder metallurgy or by melting. Homogeneity means complete diffusion during the sintering of the alloys which are prepared by powder metallurgy. It has been found from experience that the best criterion for establishing the completeness of diffusion is the sharpness of the X-ray diffraction patterns. This criterion has been used throughout the present study.

The X-ray diffraction data were obtained using powder cameras of either 214.86 or 71.62 mm diam. Copper, cobalt, or chromium K $\alpha$  radiation was used, the choice being based on the alloy composition. The powder samples were obtained by filing or crushing, depending on whether the alloy was ductile or brittle. In some cases, the powder was annealed for 4 to 6 hr at 1200°F in vacuum. The measurements were corrected for film shrinkage and absorption. The large camera, in which the film is mounted

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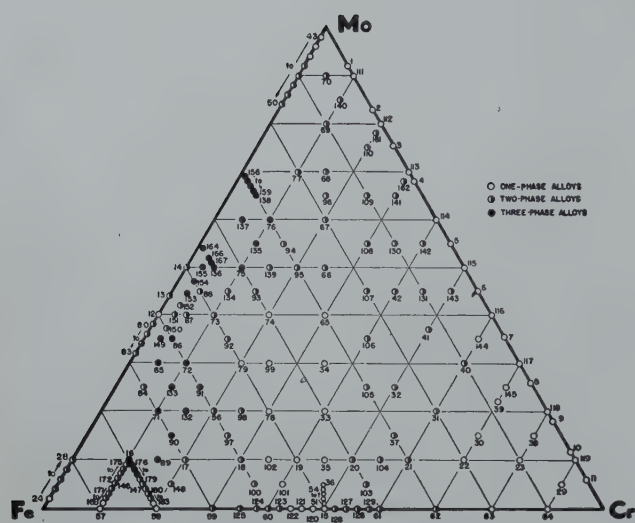


Fig. 1—Ternary diagram showing composition of alloys in atomic percentage.

symmetrically with respect to the X-ray beam, was calibrated with calcite. For the small camera, film shrinkage automatically was taken into account by mounting the film assymmetrically, the Straumanis technique. Absorption corrections were made following the graphical extrapolation method recently described by Nelson and Riley.<sup>4</sup> This technique was found more expeditious than the more generally used Cohen's method.

### Binary Systems

Although the three binary systems have been established previously, binary alloys were prepared in order to obtain additional X-ray diffraction data and to check the phase boundaries at 1200°F.

Phase boundaries which involve the  $\sigma$  phase in the Fe-Cr binary system have been located most reliably by Cook and Jones.<sup>5</sup> The present study confirmed their results by establishing from X-ray diffraction measurements that at 1200°F the  $\sigma$  phase extends from 43 to 50 atomic pct Cr. The end points of the two-phase regions were located near 30 and 71 atomic pct Cr. These results agree closely with those of Cook and Jones and furnish new evidence that the  $\sigma$  phase extends closer to both iron and chromium than was indicated by previous investigators, see, for example, ref. 6.

The generally accepted phase diagram for the Fe-

Mo system<sup>7</sup> is a compromise between the results obtained by Sykes<sup>8</sup> and by Takei and Murakami.<sup>9</sup> The most important points which have a bearing on the present work are the solubility limits at both ends of the diagram at 1200°F and the exact location of the  $\epsilon$  phase. The solubility of iron in molybdenum was determined by plotting the lattice parameter of alloys 43 through 50 vs. composition. The solubility limit was located at 8 atomic pct Fe. The same procedure applied to alloys 24 through 28 indicated that the solubility of molybdenum in iron is 4 atomic pct. These results confirm the location of the phase boundaries of the equilibrium diagram given in ref. 7.

The  $\epsilon$  phase of the Fe-Mo system has been located by Sykes<sup>8</sup> between 39 and 40 atomic pct Mo. The upper boundary corresponds to the formula  $\text{Fe}_3\text{Mo}_2$ . Arnfelt and Westgren<sup>10</sup> found the structure of this phase to be rhombohedral  $D_{3d}$  with  $a = 8.97 \text{ \AA}$  and  $\alpha = 30^\circ 38.6'$ . These investigators proposed the formula  $\text{Fe}_2\text{Mo}_3$  because this structure requires 13 atoms per cell. The rhombohedral structure of the  $\epsilon$  phase was confirmed by the present investigation for alloy 12, which has an  $\text{Fe}_3\text{Mo}_2$  composition. Alloy 13, which corresponds to  $\text{Fe}_2\text{Mo}_3$ , and alloy 14, which corresponds to  $\text{FeMo}$ , showed characteristic diffraction lines of the molybdenum-rich  $\alpha$  solid solution. Alloys 80 through 83 were examined and found to contain the  $\epsilon$  phase with the same parameters. The iron-rich solid solution was detected in alloys 83, 82, and 81, and microscopic investigation revealed that alloy 80 consisted of two phases. It was concluded that the  $\epsilon$  phase is located near the  $\text{Fe}_3\text{Mo}_2$  composition and extends less than 2 pct towards iron. The stoichiometric composition  $\text{Fe}_2\text{Mo}_3$ , which characterizes the crystal structure of  $\epsilon$ , is not inside the phase boundaries of the single-phase region. This anomaly has been found in several alloy systems.

The Cr-Mo system has been investigated by Trzebiatowski,<sup>11</sup> who showed that the two metals form an uninterrupted series of solid solutions. These results were confirmed and the variation of lattice parameter vs. composition is shown in Fig. 2. The small difference between the present results and those given by Trzebiatowski has no obvious explanation. The possible existence of a phase of the  $\sigma$  type or of an ordering reaction in the Cr-Mo system was investigated by heat treating the alloys for 6 weeks at 1200°F. The powder patterns obtained after this treatment indicated only the presence of the  $\alpha$  phase.

### Ternary System

The cross-section of the ternary-phase diagram at 1200°F is given in Fig. 3. The contours of equal lattice parameter in the  $\alpha$ -solid solution regions are labeled in A units. In the  $\sigma$ -phase region the parameter given in Fig. 3 is that of the smallest axis of the tetragonal cell of  $\sigma$ .† The ternary diagram is also presented in Fig. 4, in which the compositions are given in weight percentages. A few interesting details concerning the location of some of the phase boundaries are discussed below.

**Phase Boundaries of the  $\alpha + \sigma$  Region:** The phase boundaries of the  $\alpha + \sigma$  region were established by locating the intersection of the tie lines in this two-phase region with the lines of the constant lattice parameter in the  $\sigma$  and  $\alpha$  fields. The accuracy of a

† A tentative unit cell for the  $\sigma$  structure and a more detailed discussion of the  $\sigma$  field are given in ref. 12.

Table I. Data on Metal Powders

| Metal      | Source                                                                         | Mesh Size | Analysis, Pct                                                                      |
|------------|--------------------------------------------------------------------------------|-----------|------------------------------------------------------------------------------------|
| Iron       | Carbonyl iron, type L<br>Charles Hardy, Inc.<br>420 Lexington Ave.<br>New York | —325      | 0.008 C<br>0.05 Si<br>0.05 Mn<br>0.05 Ca<br>Traces of Ni, Cu, Mo, Ti, and Cr       |
| Chromium   | Electrolytic grade<br>Charles Hardy, Inc.                                      | —300      | 0.1 Na<br>0.05 Ca<br>Traces of Cu, Al, Mg, Si, Co, and Mn                          |
| Molybdenum | Reduced from molybdic acid                                                     | —200      | 0.25 Fe<br>0.1 Ni<br>0.05 Ca<br>0.05 Cr<br>0.05 Mn<br>Traces of Ti, Co, Ba, and Sr |



phase boundary which is determined by this method depends on the angle of intersection of the tie lines in the two-phase region with the parameter contours in a one-phase region. The best conditions are achieved when this angle is near  $90^\circ$ . In the particular case of the boundary between the  $\alpha$  and the  $\alpha + \sigma$  fields, see Fig. 3, the uncertainty in the position of the phase boundary is rather large for molybdenum concentration less than about 25 atomic pct, since in this region the parameter contours intersect at a small angle.

The X-ray diffraction patterns of the alloys which are located in the  $\alpha + \sigma$  field clearly revealed the presence of the two phases, with two exceptions. The  $\alpha$  phase was not observed in the diffraction patterns of alloys 105 and 20. However, microscopic observation confirmed the existence of the  $\alpha$  phase in these alloys. As an example, the structure of alloy 20 (40 pct Fe, 50 pct Cr, and 10 pct Mo) containing  $\alpha$  and  $\sigma$  phases is shown in Fig. 5a. The X-ray diffraction patterns of some of the two-phase alloys did not always reflect the correct proportions of  $\sigma$  and  $\alpha$ . For example, the intensity of the  $\sigma$  pattern of alloys 31, 21, and 37 was very weak, although the relative proportion of  $\sigma$  in these alloys, see Fig. 3, should be approximately 25, 50, and 75 pct, respectively. It is of course quite possible that the powder sample mounted in the camera did not contain the true proportion of  $\alpha$  and  $\sigma$ . Quantitative X-ray diffraction analysis is particularly difficult in the present case of a very brittle phase dispersed in a ductile matrix.

**Phase Boundaries of the  $\alpha + \epsilon$  and the  $\alpha + \epsilon + \sigma$  Fields:** The complicated diffraction pattern of  $\epsilon$  superimposed on the equally complicated pattern of  $\sigma$  presented a practical difficulty in interpreting the structure of several ternary alloys in a region of low chromium content. Where only a small proportion of  $\epsilon$  existed with a large proportion of  $\sigma$ , or vice versa, it was difficult to ascertain the presence of the minor constituent. For example,  $\sigma$  was not detected in alloys 153 and 154, and the presence of  $\epsilon$  was questionable in alloys 75 and 137. The proof that these alloys actually are located in a three-phase region was based on the invariancy of the lattice parameters of the two observed phases.

The boundary between the  $\alpha + \epsilon$  region and the  $\alpha + \epsilon + \sigma$  region was located parallel to the Mo-Fe side of the diagram and within less than 1 pct Cr, because alloys 156 and 164, which contain 1 atomic

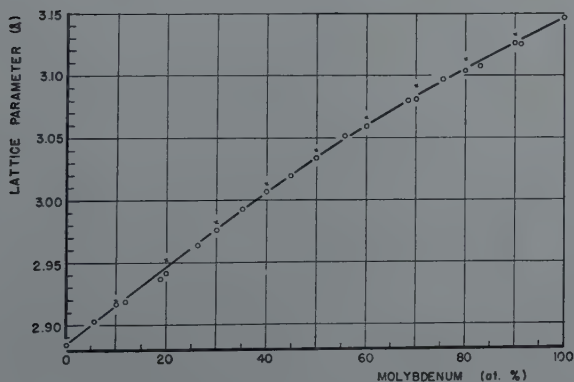


Fig. 2—Lattice parameter vs. composition of Cr-Mo binary alloys.

O—This investigation. X—Trzebiatowski.<sup>11</sup>

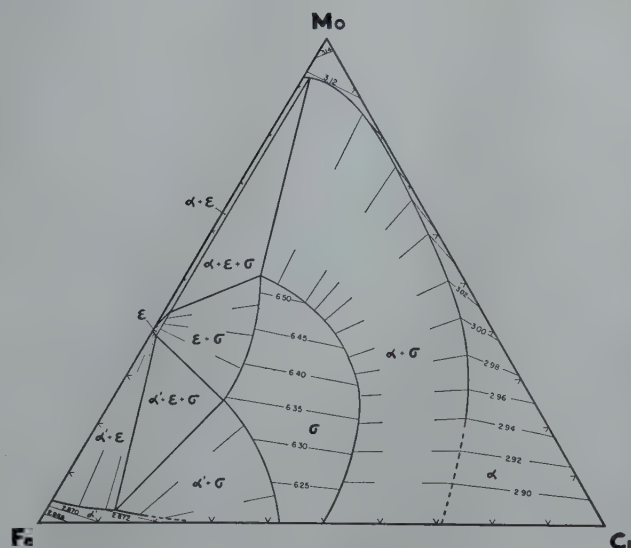


Fig. 3—Phase boundaries in ternary Fe-Cr-Mo diagram at  $1200^\circ\text{F}$  ( $650^\circ\text{C}$ ). Compositions are in atomic percentages.

pct Cr, contained three phases. The intersection of this boundary and the parameter contour of 3.125 Å in the  $\alpha$  single-phase region established the  $\alpha$  apex of the  $\alpha + \epsilon + \sigma$  triangle. The lattice parameter of the  $\alpha$  phase in alloys which consisted of three phases was 3.125 Å.

The  $\epsilon$  apex of the  $\alpha + \epsilon + \sigma$  triangle was determined from the results obtained on a series of alloys which contained 2 atomic pct Cr (Nos. 151 through 155). Alloys 153, 154, and 155 contained three phases, while alloys 152 and 88 contained only two phases and were approximately on the same tie line in the  $\epsilon + \sigma$  region. From these results, the  $\epsilon$  apex was located at approximately 54 pct Fe, 45 pct Mo, and 1 pct Cr.

The boundary between the  $\alpha + \sigma$  region and the  $\alpha + \epsilon + \sigma$  region was established on the basis of the  $\alpha$  apex of the three-phase triangle and the nearest known tie line in the  $\alpha + \sigma$  region. The apex of the three-phase region was located so that it would fall on the correct lattice parameter contour of the one-phase  $\sigma$  region.

**Fe-Rich Corner:** In the Fe-rich corner of the ternary system, the X-ray diffraction method was supplemented by microscopy. In this region, it was difficult to determine accurate contour lines because of the small variation in lattice parameter with composition. Hence, the phase boundaries in the vicinity of the  $\alpha'$  apex of the  $\alpha' + \epsilon + \sigma$  region were located approximately from X-ray data, then a series of additional alloys, Nos. 168 through 185, were prepared for metallographic observation. The boundary between the  $\alpha'$  region and the  $\alpha' + \epsilon$  region was located between alloys 168 and 169, namely, between 1 and 2 pct Mo on the 10 pct Cr line. The structures of alloys 168 ( $\alpha'$ ) and 169 ( $\alpha' + \epsilon$ ) are shown in Fig. 5b and 5c. By the same method, the boundary between the  $\alpha' + \epsilon$  region and the  $\alpha' + \epsilon + \sigma$  region was found between alloys 174 and 175 and was traced as shown on Fig. 3. This boundary intersects the 10 pct Cr line near 9 pct Mo.

Alloys 178, 179, and 147 were used for the determination of the boundary between the  $\alpha' + \sigma$  region and the  $\alpha' + \epsilon + \sigma$  region. The structure of alloy 178 revealed three phases with the  $\epsilon$  phase distributed in a matrix of  $\alpha'$  and with the  $\sigma$  phase

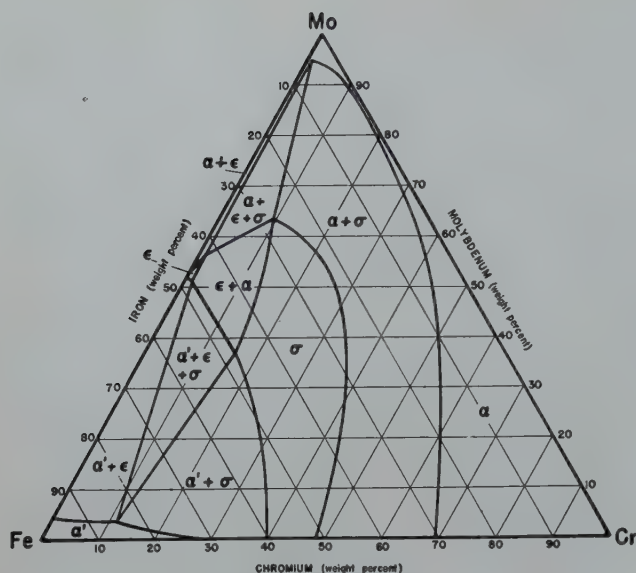


Fig. 4—Phase boundaries in Fe-Cr-Mo ternary diagram at 1200°F (650°C). Compositions are in weight percentages.

at the grain boundaries. In alloy 179 the  $\sigma$  phase was precipitated at the grain boundaries. An X-ray diffraction pattern of alloy 147 showed very weak lines of the  $\sigma$  phase. As a result of these observations, the boundary between the  $\alpha' + \sigma$  region and the  $\alpha' + \sigma + \epsilon$  region was located near 6 pct Mo on the 80 pct Fe line.

A comparison of the structure of alloys 182 and 183 led to the conclusion that the boundary between the  $\alpha'$  region and the  $\alpha' + \sigma$  region passes through a point between 1 and 2 pct Mo on the 80 pct Fe line. The boundary between the  $\alpha' + \sigma$  region and the  $\sigma$  region was based on the structures of alloys 17, 18, 56, 97, 98, 100, and 148. The microstructure of all these alloys clearly indicated the presence of the two phases. The X-ray diffraction results confirmed the presence of the two phases, except for alloy 98 in which no body-centered phase ( $\alpha'$ ) was detected. The tie lines in the  $\alpha' + \sigma$  region were determined by the X-ray method. The boundary was drawn through the points of intersection of these lines with the parameter contours in the  $\sigma$ -phase field. It was then found that alloy 98 is very near the  $\sigma$  field and a cubic body-centered diffrac-

tion pattern was not observed because the amount of  $\alpha'$  was less than about 2 pct.

**Three-Phase Region  $\alpha' + \epsilon + \sigma$ :** As in the case of the  $\alpha + \epsilon + \sigma$  region, the simultaneous presence of  $\sigma$  and  $\epsilon$  caused some complications in analyzing the X-ray diffraction patterns of the three-phase alloys. The  $\epsilon$  pattern was present in all the alloys located in this field, except in alloy 91. The  $\alpha'$  phase also was observed clearly in all alloys, except No. 86. The invariance of lattice parameters was used as a further check for the three-phase alloy. The parameters of the  $\epsilon$  phase were very near that of the  $\epsilon$  phase in the binary Fe-Mo system; hence the  $\epsilon$  apex was located at 1 pct Cr.

The boundary between the  $\alpha' + \sigma$  region and the  $\alpha' + \epsilon + \sigma$  region was drawn through the 6 pct Mo, 80 pct Fe point, which was discussed above. This boundary was drawn with a slope such that it would include alloy 89 in the three-phase region and exclude alloy 56, which was a two-phase alloy ( $\alpha' + \sigma$ ). The end point of this boundary, the  $\sigma$  apex of the three-phase region, was determined on the basis of the parameter contours in the  $\sigma$  field and the parameter of the  $\sigma$  phase, which was present in the three-phase alloys.

The phase boundary between the two-phase region  $\epsilon + \sigma$  and the one-phase  $\sigma$  region was drawn as a smooth curve between the  $\sigma$  apexes of the two three-phase regions. The use of tie lines and parameter contours was not possible because of their near parallelism. Microscopic observation was also very difficult because the alloys which are located in this region were very porous and brittle. The location of the boundary, however, was substantiated by the observations that alloys 92 and 93 contained two phases, while alloys 74 and 79 contained only the  $\sigma$  phase.

**Accuracy in Location of Phase Boundaries:** Many different factors have an influence on the accuracy of the location of phase boundaries in a ternary system. The relative importance of the various sources of error change with alloy composition throughout the diagram. As a result, the overall accuracy in phase boundary determination varies from one region of the diagram to another, and it is practically impossible to make a definite statement about the width of the region of uncertainty associated with phase boundaries. In the present case, it is believed that the uncertainty does not

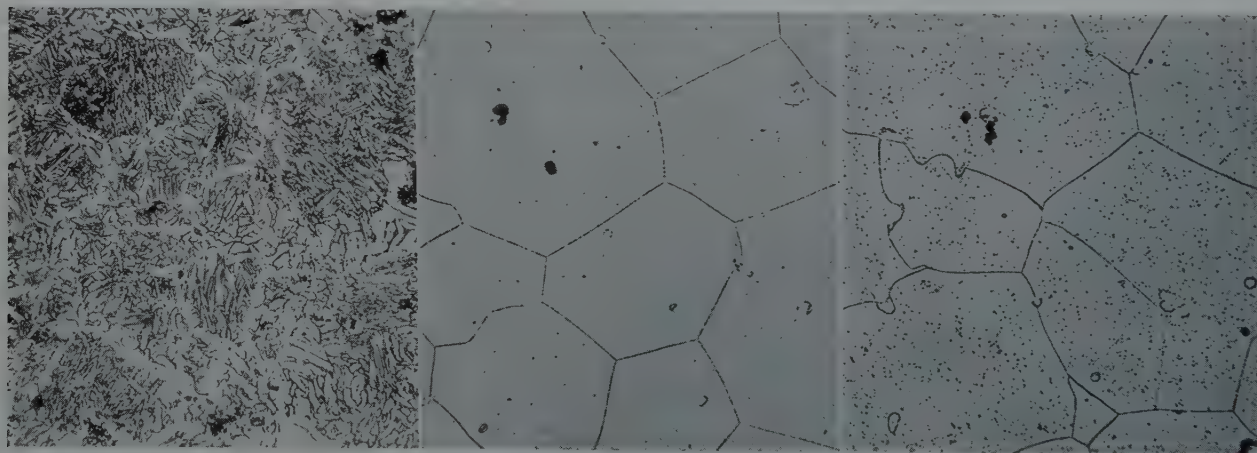


Fig. 5—Typical structures of three alloys.

a (left)—Alloy 20 ( $\alpha + \sigma$ ). b (center)—Alloy 168 ( $\alpha'$ ). c (right)—Alloy 169 ( $\alpha' + \epsilon$ ).



exceed 2 atomic pct and is probably not more than 1 pct in some regions of the diagram. These figures do not apply to part of the boundaries between  $\alpha$ ,  $\alpha + \sigma$ , and  $\sigma$  phases near the Fe-Cr side of the diagram. The uncertainty of these boundaries, which are dotted on Fig. 3, may be greater than 2 pct because some of the alloys in this region may not have reached equilibrium at 1200°F. The most logical method for improving the results in this region would be to make a study of the isothermal transformation of  $\alpha$  into  $\sigma$ , so that the attainment of equilibrium can be established definitely.

### Summary

The phase boundaries of the Fe-Cr-Mo ternary system have been determined at 1200°F (650°C). The method used for locating the phase boundaries consisted of measuring lattice parameters of the various phases and drawing the parameter contours and the tie lines in the one-phase and two-phase regions, respectively. The brittle  $\sigma$  and  $\epsilon$  phases extend over a major portion of the diagram. The largest one-phase solid solution region is located near the chromium corner of the diagram.

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### Technical Note

## Titanium-Boron Alloys

by H. R. Ogden and R. I. Jaffee

AT the present time, there appear to be two conflicting opinions on the solubility of boron in titanium. P. Ehrlich<sup>1</sup> has indicated from X-ray diffraction work that boron is soluble in titanium up to TiB<sub>0.8</sub> (17.8 wt pct, 44 atomic pct). The X-ray diffraction pattern for titanium was found in compositions up to TiB<sub>0.05-0.07</sub> (1.1 to 1.6 wt pct); then, without a phase gap, superlattice lines appeared up to TiB<sub>0.8</sub>. On the other hand, Craighead, Simmons, and Eastwood<sup>2</sup> have estimated the solubility of boron in both alpha and beta titanium to be less than 0.1 wt pct, based on results of metallographic analysis.

In some recent work done at Battelle, results were obtained which shed more light on the titanium-rich end of the titanium-boron system.

Iodide-type titanium and high-purity crystalline boron were used in this investigation. The boron was prepared by hydrogen reduction of boron tri-bromide and deposition on a hot tungsten wire. The

alloys were prepared by arc melting in an argon atmosphere of 10 cm Hg pressure on a water-cooled copper hearth. The ingots were hot rolled to strip at 850°C. Alloys containing up to 1 pct B could be hot rolled. Those containing 2 pct or more B could not be hot rolled.

Metallographically, it was found that a second phase was present in alloys containing as little as 0.4 pct B, and that the quantity of second phase increased with increasing boron content. This is illustrated in Figs. 1a and 1b, which show the microstructures of a Ti-0.4B and a Ti-1B alloy annealed in argon at 850°C.

X-ray diffraction patterns of alloys containing 1 and 5 pct B revealed the presence of extra lines which correspond to the superlattice lines reported by Ehrlich.<sup>1</sup> However, no evidence was found of a shift in the lattice constants of alpha titanium indicating that there is very little, if any, solubility of boron in alpha titanium. This fact, coupled with the fact that the alloys were definitely two-phase, indicates that the extra lines are not superlattice lines, but are more probably the result of a second phase of a hexagonal structure almost identical in cell

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Fig. 1—Microstructure of various TiB alloys.

a (upper left)—Ti-0.4B alloy annealed 3 hr at 850°C. X500. b (upper right)—Ti-1B alloy annealed 3 hr at 850°C. X500. c (lower left)—Ti-0.4B alloy quenched after 4 hr at 893° ± 2°C. X250. d (lower right)—Ti-0.4B alloy quenched after 4 hr at 893° ± 2°C. X250.

dimensions with that of alpha titanium. M. Hansen<sup>3</sup> has suggested that the titanium superlattice reported by Ehrlich may be a hexagonal-close-packed intermediate phase based on Ti<sub>2</sub>B. With this interpretation, the change in constants Ehrlich found for the hexagonal lattice would belong to the first titanium-rich intermediate phase, rather than the superlattice. Furthermore, it is known from Hagg's work, that in systems of metalloids and transition elements, M<sub>2</sub>X phases are usually hexagonal-close-packed.<sup>4</sup> This would account for the Ti<sub>2</sub>B structure in this system being hexagonal. Also, from the relative size of the interstitial elements, one would expect boron to have a lower solubility than carbon, which has been found to be about 0.5 wt pct maximum at the peritectoid temperature.<sup>5</sup>

Additional metallographic work has shown that boron additions do not measurably affect the transformation temperature of titanium. Figs. 1c and 1d show the structures of a Ti-0.4B alloy heated in argon and quenched in water from 880° and 893°C. At 880°C just below the 882°C transition temperature of titanium, the structure is alpha plus boride, while at 893°C, just above the transition of pure titanium, the structure is beta plus boride. This follows from the appearance of the alpha grains

after quenching. The transformation product of the beta phase consists of serrated Widmanstätten alpha plates, which are similar to those found in beta-quenched iodide titanium.<sup>5</sup>

The mechanical properties of the titanium-boron alloys used in this investigation also were obtained and are given in Table I. The addition of boron to titanium increases the strength only a moderate amount, but also decreases the ductility progressively. This is the type of effect that would be expected when a dispersed intermetallic phase is present in the structure.

It can be concluded from these data that the solubility of boron in both alpha and beta titanium is probably very low, well below 0.4 pct B, and that boron has no observable effect on the transition temperature of titanium. Furthermore, the hexagonal-close-packed structure of the second phase indicates that it is probably of the M<sub>2</sub>X type or Ti<sub>2</sub>B.

### Acknowledgment

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- <sup>5</sup>R. I. Jaffee, H. R. Ogden, and D. J. Maykuth: The Alloys of Titanium with Carbon, Oxygen, and Nitrogen. *Trans. AIME* (1950) 188, p. 1261; *JOURNAL OF METALS* (Oct. 1950).

Table I. Mechanical Properties of Titanium-Boron Alloys

| Composition, B, Pct | Proportional Limit, Psi | 0.2 Pct Offset Yield Strength, Psi | Ultimate Strength, Psi | Elongation, Pct, 1 In. |
|---------------------|-------------------------|------------------------------------|------------------------|------------------------|
| 0                   | 11,000                  | 27,000                             | 43,000                 | 40                     |
| 0.4                 | 21,000                  | 48,000                             | 71,000                 | 20                     |
| 1.0                 | 22,000                  | 44,000                             | 65,000                 | 4                      |



# Extraction of Alumina from Haiti and Jamaica Bauxites

by T. D. Tiemann

The chemical and mineralogical composition of Caribbean bauxite ores are described. Extraction of alumina by several processes from both Haiti and Jamaica bauxites is discussed and data presented.

IMMENSE deposits of bauxite occur in the Caribbean islands of Hispaniola and Jamaica in the high plateau lands and have been excellently described by O. C. Schmedeman.<sup>1</sup> The bauxite occurs as deposits in catchments or etched depressions in Tertiary limestone believed to have been deposited in the Eocene and Oligocene periods.<sup>2</sup> In appearance both the Haiti and Jamaica bauxites resemble a relatively high iron clay and have indeed been mistaken for such.<sup>3</sup> They are very soft and friable and disperse readily on vigorous agitation in water. The color range in general is light brown to red.

Chemically, the outstanding characteristic of the bauxites is the low silica and high ferric oxide content. The extremely low silica makes them particularly valuable for the production of alumina in the Bayer plant since silica is responsible for the loss of both alumina and soda chemically combined as  $XNa_2O \cdot YSiO_2 \cdot ZAl_2O_3$ . The ferric oxide, only traces of ferrous iron are present, offers no interference in the production of high grade alumina. Typical oxide analyses of three types of ore are given in Table I<sup>2</sup> and a list of the elements occurring in spectrographic quantities in Table II.<sup>3</sup>

The size of the individual particles in the ore makes successful petrographic examination extremely difficult. The ores contain some relatively coarse grains of heavy minerals such as ilmenite, magnetite, and rutile, but other than occasional crystals of a few microns, the greater portion of the minerals are submicroscopic in size and approach colloidal dimensions.

The mineralogic composition of the ores has been investigated by X-ray and differential thermal analysis.<sup>4</sup> These investigations indicate that the predominant mineral phases present are gibbsite ( $Al_2O_3 \cdot 3H_2O$ ), boehmite ( $Al_2O_3 \cdot H_2O$ ), hematite ( $Fe_2O_3$ ), and goethite ( $Fe_2O_3 \cdot H_2O$ ). There is no evidence of the occurrence of diaspore ( $Al_2O_3 \cdot H_2O$ ) in either the Haiti or Jamaica ores, but some type of "amorphous" alumina may be present in some of the bauxites of Jamaica.<sup>4</sup>

The temperature stability regions in the alumina-water system have been investigated and are given in recent literature. In the temperature range where the hydrated forms are stable, as determined by

hydrothermal bomb methods,<sup>5</sup> gibbsite is the stable phase to 155°C (311°F), boehmite from 155°C (311°F) to 280°C (536°F), and diaspore from 280°C (536°F) to 450°C (842°F).

Although quite similar in many characteristics, the Haiti and Jamaica ore show a divergence in mineralogic composition that is reflected in the extractability of the alumina described in later paragraphs. Two principal differences occur in mineralogic composition. The iron-bearing mineral in the Haiti ores is predominantly hematite, while in the Jamaica ores goethite is predominant.<sup>4</sup> Directly related to the extraction of alumina are the two minerals, gibbsite and boehmite. Boehmite is relatively high in the Haiti ores and in some of the less soluble Jamaica ores, while gibbsite predominates in the ores in Jamaica amenable to the American Bayer process of extraction.

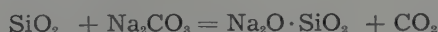
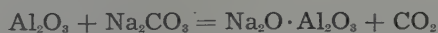
## Pedersen and Related Processes

In general, all processes for the extraction of alumina involving sintering or fusion of bauxite ores with limestone, soda ash, or a combination of limestone and soda ash followed by leaching, are based on the formation of alumina compounds that yield alumina soluble in the subsequent leach.

The principal idealized reactions in respect to alumina and silica for the three types of processes are as follows:

### Soda Ash

#### Sinter:

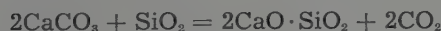
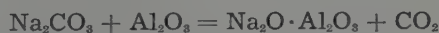


#### Leach (with excess water):



### Soda Ash — Limestone

#### Sinter:



#### Leach (with excess water):



These latter reactions are the basis of the sinter process currently used for the recovery of soda and

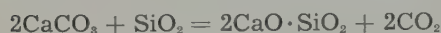
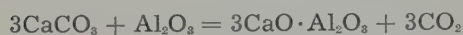
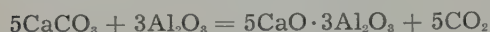
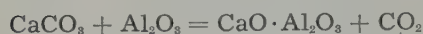
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Discussion of this paper, TP 3032D, may be sent (2 copies) to AIME by July 1, 1951. Manuscript, Sept. 7, 1950. St. Louis Meeting, February 1951.

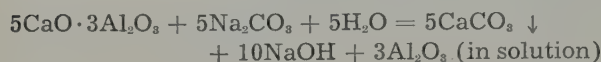
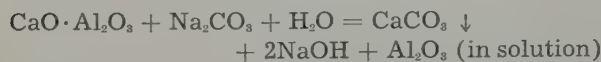
alumina from the mud residues of the Bayer circuit.

#### Limestone

Sinter (modified Pedersen):



Leach (with excess water):



It will be noted that in the reaction with soda ash and limestone, the principal function of lime is to combine with the silica, thus liberating both alumina and soda which would otherwise be lost in the relatively insoluble sodium aluminum silicate; further, the combination of lime with silica decreases the silica taken into solution in the leach.

The original Pedersen process is based on the electrothermal fusion and simultaneous reduction of the iron oxide in the ore with coke to form as products metallic iron and a high alumina slag which is subsequently leached. The reactions in respect to calcium carbonate, alumina, and silica are, however, as indicated above.

In the Pedersen processes, formation of dicalcium silicate serves a dual purpose. The extraction of silica in the leach is lowered, and, if the compound composition and conditions of burning and cooling are correctly controlled, the beta-dicalcium silicate

formed at the high burning temperature (1200° to 1400°C) inverts on cooling to the gamma phase stable below 675°C.<sup>6</sup> This inversion takes place with a 10 pct increase in volume<sup>6</sup> which disintegrates the sinter or fusion, eliminating the necessity of grinding before the leach. This inversion causes the well-known "dusting" of the Portland cement industry.

In all of these types of treatment, the alumina is recovered from solution by precipitation with carbon dioxide liberated in the sintering stage. The sodium carbonate thus formed is recycled.

The silica content of the filtrate from the leach is considerably higher than in the Bayer processes, and usually some means of desilication must be employed preceding the precipitation of alumina.

Detailed descriptions of these processes are to be found in the literature. A rather complete description is given in a paper<sup>7</sup> on the application of the sinter methods to the treatment of clays.

*Application to Haiti Ores:* A rather extensive series of laboratory tests was made during the early investigation on Haiti bauxites to determine the possibility of applying these methods to the extraction of alumina. The greater part of the investigation was devoted to Pedersen treatment by both sintering and fusion methods.

Furnace treatment covered a temperature range of 1000° to 1500°C under both oxidizing and reducing conditions. The compositions in respect to CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> covered the greater part of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> equilibrium diagram below 15 pct SiO<sub>2</sub>, ranging in CaO from 20 to 65 pct. Quenching in air or water as well as slow cooling was used.

Leaching conditions were investigated over a wide range in respect to concentrations, time, and temperature, and it was found that a leach of 30 min at 50°C using a 3 pct sodium carbonate solution in the ratio of one liter of solution to 25 g of sinter gave the most consistent results.

Although over 300 separate burns were made, the phenomenon of "dusting" was observed in only a few cases even with addition of silica.

Extractions\* of alumina were very inconsistent and in most cases were below 60 pct. Some extractions of 95 pct or greater were obtained, but these only under highly reducing conditions and at temperatures around 1300° to 1400°C. No quantitative relationship between composition with respect to CaO and extraction could be established. The very few cases of "dusting" encountered may have been due to the small amount of beta-dicalcium silicate formed in the low silica burns. However, in the burns made with the addition of silica, petrographic examination showed the presence of considerable beta-dicalcium silicate. It is known<sup>6</sup> that small amounts of oxides, among which may be mentioned B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, in solid solution in the dicalcium silicate may prevent the beta to gamma inversion. This may be in part the reason for the apparent stability of the beta phase in the high silica tests.

A reaction not shown in the former discussion on sinter and fusion processes is that of CaO, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>. These three oxides in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system may combine to form tetracalcium aluminoferrite (4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>), a compound that is of common occurrence in both Port-

\* The term "extraction" as used throughout the discussion refers to results of laboratory tests. Actual plant recoveries of metal-grade alumina are estimated to be about 95 pct of the laboratory extractions.

Table I. Oxide Analyses of Typical Caribbean Bauxite Ores, Pct

| Bauxite                                   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | MnO  | Loss on Ignition | Total |
|-------------------------------------------|------------------|--------------------------------|--------------------------------|------------------|-------------------------------|------|------------------|-------|
| Jamaica (high alumina solubility)         | 0.29             | 48.00                          | 21.06                          | 2.33             | 0.03                          | 0.12 | 27.46            | 99.29 |
| Jamaica (intermediate alumina solubility) | 0.70             | 48.50                          | 20.94                          | 2.25             | 0.41                          | 0.15 | 26.11            | 99.06 |
| Haiti (low alumina solubility)            | 3.89             | 47.92                          | 21.61                          | 2.80             | 0.43                          | 0.24 | 22.28            | 99.17 |

Table II. Trace Elements Occurring in Caribbean Bauxite Ores, Semiquantitative Spectrographic Analysis

| Range in Percent | Jamaica Bauxite               | Haiti Bauxite                     |
|------------------|-------------------------------|-----------------------------------|
| 0.1-1.0          | Mg                            | Ca, Mg                            |
| 0.01-0.1         | Cr, Mn, Ca, Sr, Ni, Zr, V, Mo | Mn, Cr, Ni, Zr, V, Sr, Cu, Pb, Mo |
| 0.001-0.01       | Pb, Ba, B                     | Ba, B                             |

Table III. Extraction vs. Digestion Time of Jamaica Bauxite of High Alumina Solubility

| Time, Min | Alumina Extraction, Pct |
|-----------|-------------------------|
| 15        | 97                      |
| 30        | 96                      |
| 60        | 96                      |



land and high alumina cements. If this compound formed, each mol of  $\text{Fe}_2\text{O}_3$  would combine with a mol of  $\text{Al}_2\text{O}_3$  and since these bauxites contain on the order of 20 pct  $\text{Fe}_2\text{O}_3$  and 48 pct  $\text{Al}_2\text{O}_3$ , approximately 27 pct of the alumina content would be lost in the extraction residue, allowing a maximum extraction of alumina of only 73 pct.

Consequently, with bauxite low in silica and high in ferric oxide, extraction of alumina may be low. An increase in extraction may result under reducing conditions where a substantial portion of  $\text{Fe}_2\text{O}_3$  is converted to  $\text{FeO}$ , or as in the original Pedersen fusion process converted to metallic iron. Application of the Pedersen processes to the treatment of these bauxites is felt to be entirely unsatisfactory from both technical and economic considerations.

Treatment by the soda ash and soda ash-lime-stone processes was also investigated.

High extractions of both soda and alumina (95 pct) were consistently obtained by sintering around  $1200^\circ\text{C}$ , followed by leaching for 30 min in water (100 g of sinter per liter) at  $50^\circ\text{C}$ . Solutions and alumina obtained from these tests were relatively high in silica content, indicating the need of a desilication step in a process employing these methods.

This type of extraction, though technically feasible, is doubtful from an economic standpoint as compared to treatment of these Haiti bauxites by a modified European Bayer process to be described.

### Bayer Processes

The principle of the Bayer process is based on the change in solubility of alumina in caustic solutions with variation in temperature. The solution, \*\* which is saturated with respect to alumina at digestion temperature, becomes supersaturated on subsequent cooling and precipitates alumina to the lower more stable concentration of the precipitation temperature. Precipitation is initiated by "seeding" with nuclei of alumina trihydrate.

These concentration levels are usually defined by the weight ratio of alumina in solution to caustic in solution expressed as free soda.† In normal plant operation, the lower stable concentration at precipitation temperature is represented by a ratio of about 0.30, while the ratio corresponding to the supersaturated level is around 0.57 to 0.58. Thus the weight of alumina produced per unit volume is represented by the difference of the two ratios or about 0.28 times the free soda concentrations. Decrease in the upper ratio represents decrease in production or a larger capacity requirement for the same production.

Although under special laboratory conditions high supersaturation can be attained, a limit corresponding to a ratio of around 0.60 is imposed in plant operation due to the danger of spontaneous precipitation on cooling from digestion temperatures.

The American Bayer process employs digestion temperatures in the region of  $290^\circ\text{F}$  and caustic concentrations of about 140 g per liter free soda while in the European Bayer process digestion temperatures as high as  $350^\circ\text{F}$  and caustic concentrations as high as 600 g per liter free soda may be

Table IV. Alumina Extraction vs. Digestion Temperature and Caustic Concentration of Jamaica Bauxite of Intermediate Alumina Solubility

| Caustic Concentration, Free Soda, G per Liter | Digestion Temperature, $^\circ\text{F}$ | * Alumina Extraction, Pct |
|-----------------------------------------------|-----------------------------------------|---------------------------|
| 140                                           | 290                                     | 80                        |
|                                               | 320                                     | 80                        |
|                                               | 340                                     | 80                        |
|                                               | 360                                     | 80                        |
|                                               | 380                                     | 80                        |
|                                               | 400                                     | 89                        |
| 250                                           | 290                                     | 81                        |
|                                               | 320                                     | 81                        |
|                                               | 340                                     | 81                        |
|                                               | 360                                     | 84                        |
|                                               | 380                                     | 89                        |
|                                               | 400                                     | 91                        |
| 480                                           | 290                                     | 84                        |
|                                               | 320                                     | 86                        |
|                                               | 340                                     | 90                        |
|                                               | 360                                     | 92                        |
|                                               | 380                                     | 93                        |
|                                               | 400                                     | 93                        |

used. An excellent discussion of this and other processes is given by R. S. Sherwin.<sup>8</sup>

*Application to Haiti and Jamaica Bauxites:* Under the mineralogic composition of these bauxites was mentioned a relation between the extraction of alumina and the relative mineral content of gibbsite and boehmite. The ores in Jamaica vary from a type high in gibbsite, from which the alumina is readily extracted, to ores containing mixtures of gibbsite and boehmite requiring higher temperatures and caustic concentrations to obtain suitable alumina recovery.

The Haiti bauxites are essentially of this latter type and require conditions of digestion approaching those of European Bayer practice, which in this paper is termed Modified European Bayer. No Jamaica ores examined so far in this laboratory have been found in which the alumina is as insoluble as that in the Haiti ores.

*Jamaica Bauxite of High Alumina Solubility:* Investigation of the digestion characteristics of the Jamaica ores has delineated an extremely large tonnage that is readily amenable to treatment under American Bayer conditions of digestion temperature and caustic concentration. It is to be noted that this type in general shows a loss on ignition of 27 pct or greater.

Loss on ignition in itself, however, is not the final criterion of alumina solubility since it may be related in part to organic content and hydration of minerals other than those of alumina.

This bauxite consistently gives extractions of 95 pct or higher of the total alumina content at saturation ratios (alumina:free soda) of 0.58 to 0.60. This amounts to almost complete extraction of the so-called available alumina‡ (theoretical maximum extractable alumina), and hence no increase in either temperature or caustic concentration will yield substantially higher alumina extractions.

It is perhaps advisable at this point in the discussion to mention the important fact that grinding is unnecessary to high yields of alumina due to the extremely fine size of the bauxite particles.

Closely related to the state of subdivision is the relation of time of digestion to alumina extraction. Many tests have indicated that time is not an important factor as far as alumina solubility is concerned and under any given conditions of tempera-

\*\* The term "solution" as used here includes colloidal as well as ionic and molecular solution.

† Free soda is equivalent to sodium hydroxide expressed as sodium carbonate. Thus 140 g per liter free soda  $\approx$  106 g per liter NaOH.

‡ Calculated available alumina is equal to the alumina in the bauxite less  $1.2 \times \text{SiO}_2$  content.

Table V. Extraction vs. Discharge Ratios, Haiti Bauxite

| Discharge Ratio,<br>Al <sub>2</sub> O <sub>3</sub> :Free Soda | Alumina<br>Extraction,<br>Pct |
|---------------------------------------------------------------|-------------------------------|
| 0.38                                                          | 72                            |
| 0.44                                                          | 63                            |
| 0.52                                                          | 61                            |
| 0.55                                                          | 56                            |
| 0.57                                                          | 17                            |

Digestion Temperature, 290°; Free Soda, 140 g per liter

ture and caustic concentration, the rate of solubility is relatively rapid. However, in normal plant practice, a period of at least 30 min is considered necessary for proper desilication. These relations are illustrated in the data of Table III which show the extraction of alumina relative to the time of digestion for these bauxites. The temperature for these data was 290°F and the caustic concentration 140 g per liter free soda.

**Jamaica Bauxite of Intermediate Alumina Solubility:** A large part of the Jamaica bauxites have been found to be somewhat less amenable to alumina extraction than the type previously discussed. These ores might be considered to be on the economic borderline of American Bayer practice. This ore quite generally shows a loss on ignition of around 25 to 26 pct and gives a total alumina extraction of 80 pct at saturation ratios of approximately 0.56 under American Bayer conditions.

The effect of digestion temperature as well as caustic concentration on this type of bauxite is illustrated in Table IV. In these particular tests, 93 pct extraction of total alumina represents 97 pct based on the calculated available alumina. It is interesting that neither increase in temperature nor increase in caustic concentration alone has an appreciable effect on the alumina extraction and that a change in both is required for a noticeable effect. This results in a relatively long flat portion of the extraction-temperature or extraction-caustic concentration curves parallel to the temperature or caustic concentration axis.

The cause of this has not been determined, but it may be in part related to an inversion of one min-

Table VI. Extraction vs. Temperature and Caustic Concentration, Haiti Bauxite

| Caustic Concentration,<br>Free Soda,<br>G per Liter | Digestion Temperature,<br>°F | Discharge Ratio,<br>Al <sub>2</sub> O <sub>3</sub> :Free Soda | Alumina Extraction,<br>Pct |
|-----------------------------------------------------|------------------------------|---------------------------------------------------------------|----------------------------|
| 140                                                 | 290                          | 0.48                                                          | 55                         |
|                                                     | 320                          | 0.49                                                          | 60                         |
|                                                     | 340                          | 0.50                                                          | 63                         |
|                                                     | 360                          | 0.52                                                          | 67                         |
|                                                     | 380                          | 0.55                                                          | 79                         |
|                                                     | 400                          | 0.57                                                          | 83                         |
|                                                     | 425                          | 0.58                                                          | 91                         |
| 250                                                 | 290                          | 0.50                                                          | 62                         |
|                                                     | 320                          |                                                               |                            |
|                                                     | 340                          | 0.52                                                          | 71                         |
|                                                     | 360                          |                                                               |                            |
|                                                     | 380                          | 0.57                                                          | 89                         |
|                                                     | 400                          | 0.59                                                          | 94                         |
|                                                     | 425                          |                                                               |                            |
| 480                                                 | 290                          | 0.56                                                          | 75                         |
|                                                     | 320                          | 0.60                                                          | 84                         |
|                                                     | 340                          | 0.61                                                          | 88                         |
|                                                     | 360                          | 0.62                                                          | 94                         |
|                                                     | 380                          | 0.62                                                          | 95                         |
|                                                     | 400                          | 0.61                                                          | 94                         |

eral form to another with an accompanying decrease in solubility. It is to be noted that the inversion of gibbsite to boehmite takes place at 155°C (311°F), at least in the alumina-water system. This type of ore might be considered amenable to American Bayer practice if recoveries of around 80 pct were economically acceptable. However, it is probable that this ore could be more economically processed under the conditions of the Modified European Bayer processes described below.

**Jamaica Bauxite of Low Alumina Solubility:** A few of the Jamaica bauxites investigated were found to be quite unsuitable for treatment by the American Bayer process. These ores usually show a loss on ignition of about 20 pct and give an alumina extraction of 60 pct (0.56 ratio) under American Bayer conditions.

No detailed discussion or data for this type of Jamaica ore are presented since their behavior in respect to alumina extraction is quite similar to that of the Haiti ores discussed below.

Table VII. Extraction vs. Discharge Ratios Under Modified European Bayer Conditions for Haiti Bauxite

| Discharge Ratio,<br>Al <sub>2</sub> O <sub>3</sub> :Free Soda | Alumina Extraction,<br>Pct of:       |                                                     |
|---------------------------------------------------------------|--------------------------------------|-----------------------------------------------------|
|                                                               | Total Al <sub>2</sub> O <sub>3</sub> | Calculated Available Al <sub>2</sub> O <sub>3</sub> |
| 0.40                                                          | 96                                   | 100                                                 |
| 0.60                                                          | 93                                   | 98                                                  |
| 0.62                                                          | 89                                   | 94                                                  |
| 0.64                                                          | 63                                   | 67                                                  |

**Haiti Bauxite of Low Alumina Solubility:** In comparison with the first two types of Jamaica ores already discussed, the Haiti bauxites are somewhat unique with regard to alumina extraction. These bauxites are not at all amenable to American Bayer conditions, primarily due to the higher content of boehmite and in part to the higher silica. It will be noted from the analysis in Table I that these bauxites are typified by considerably lower loss on ignition (22 pct) than that of the former types and that the silica content is of the order of 3 to 4 pct.

American Bayer extractions are very low (60 pct), and the amount of alumina which can be carried in solution in respect to the caustic concentration is entirely unsuitable, never approaching a satisfactory ratio. An attempt to increase the ratio by increasing the bauxite causes a rapid decrease in extraction. This is illustrated in Table V. These considerations show why the Haiti ores cannot be economically treated by the American Bayer process.

However, the Haiti bauxites are extremely responsive to variation in temperature and caustic concentration. These relationships are illustrated in Table VI, which shows extraction vs. temperature at several caustic concentrations.

The extractions shown in Table VI are based on total alumina, and for this particular ore 92 pct represents 100 pct extraction of the theoretical calculated available alumina.

Investigations both in the laboratory and pilot plant, in which many samples of the Haiti orebodies were tested, have indicated that the most suitable digestion conditions for economic extraction of the alumina are in the higher temperature range and higher caustic concentrations somewhat below that of European practice. These conditions will yield



an extraction of approximately 90 pct of the total alumina or approximately 95 pct of the theoretical calculated available alumina based on an average analysis for these ores.

Shown in Table VII are the extraction characteristics under these Modified European Bayer conditions of an orebody typical of the Haiti deposits.

The few Jamaica ores similar to the Haiti ores in respect to composition and extraction characteristics, as well as the Jamaica ores of intermediate alumina solubility, give results comparable to those presented in Table VII when treated by the Modified European process.

No attempt will be made to introduce in this paper a detailed discussion of the settling and thickening of the residual red muds from Haiti and Jamaica bauxites resulting in the extraction of alumina from these bauxites. Laboratory tests have shown the muds to be readily flocculated by the use of starch as in current practice, and an investigation on pilot plant scale has shown that the settling and thickening characteristics are suitable for the thickener treatment.<sup>9</sup>

### Summary and Conclusions

Alumina is economically extractable from both Haiti and Jamaica bauxite by the Bayer process. A major part of the Jamaica orebodies are suitable for American Bayer treatment.

The Haiti bauxites and some of the Jamaica bauxites are amenable to treatment by a modification of the European Bayer process at high digestion temperatures and high caustic concentrations.

It is doubtful that either the Haiti or Jamaica ores can be economically treated by any of the soda or soda-lime sintering processes. The Pedersen sinter or fusion process is not suitable to treatment of bauxites of this type.

Variations in the extractability of the alumina

from both the Haiti and Jamaica ores are related principally to the relative amounts of boehmite and gibbsite present in the bauxites.

### Acknowledgments

The author thanks R. S. Sherwin and R. S. Sherwin, Jr., for their help and suggestions in preparing this paper. Thanks are due the staff of the Research Laboratory for their cooperation in supplying much of the data.

Where not otherwise noted, the data submitted are based on investigations made by the Alumina Research Department, Reynolds Metals Co., Listerhill Plant.

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### Technical Note

## Structure of the Yellow Crystalline Fraction of Blast-Furnace Salamander

by John R. Weeks, Dan McLachlan, Jr., and John R. Lewis

**D**URING the operation of the iron blast furnace, aggregates of hard, infusible, yellow, cubic crystals frequently form in the interstices of the lining and on the hearth of the furnace. These were first examined by Wohler<sup>1</sup> and were identified by him as a complex cyanonitride of titanium, having a formula  $\text{Ti}(\text{CN})_2 \cdot 3\text{Ti}_3\text{N}_2$ , or more simply  $\text{Ti}_{10}\text{C}_2\text{N}_8$ . However, recent investigators have suggested that this complex compound does not exist. Recent work by Hume-Rothery, Raynor, and Little<sup>2</sup> on the carbide and nitride particles in titanium steels suggests that a complete series of solid solutions of the general

type  $\text{Ti}_{(10-y)}\text{C}_y\text{N}_8$  exists between titanium carbide (TiC) and titanium nitride (TiN). Assuming this to be true, it seems likely that Wohler's cyanonitride of titanium is in reality a solid solution of 20 mol pct TiC in 80 mol pct TiN, the nearly consistent carbide-to-nitride ratio probably resulting from temperature and pressure conditions in the blast furnace. The object of the present work was to investigate thoroughly this possibility of a solid solution by using the single-crystal methods of X-ray analysis.

A spectrographic qualitative analysis of a sample of the yellow crystals furnished by the Geneva Steel Co. showed, in addition to the titanium, strong lines of vanadium and moderate to weak lines of iron, magnesium, silicon, aluminum, and calcium. The last five were probably slag impurities, but the vanadium was possibly included in the yellow crystals, owing to a great structural similarity of its carbide (VC) and its nitride (VN) to the titanium compounds, Table II. A chemical analysis was made

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TN 72C. Manuscript, Feb. 12, 1951.

This paper represents part of a thesis by Mr. Weeks submitted in partial fulfillment of requirements for the degree of Master of Science to the University of Utah.

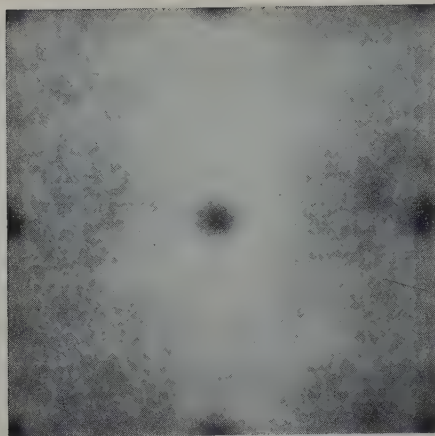
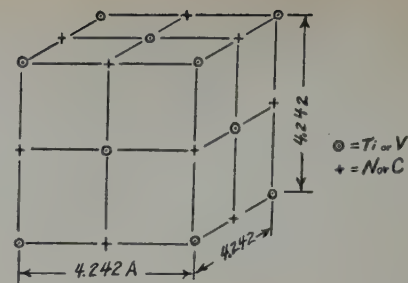


Fig. 1a (left)—Fourier projection  $\rho(x, y)$  taken of the image obtained on the screen from the multiple projector.

Fig. 1b (right)—Drawing of the calculated unit cell of the yellow crystals.



of the sample for titanium, vanadium, carbon, and nitrogen. The results are shown in Table I. These show the ratio titanium plus vanadium to carbon plus nitrogen of 1 to 1.013 and indicate strongly the substitution of vanadium for titanium in the yellow crystals. Although the nearest empirical chemical formula based on Table I  $[(\text{Ti}, \text{V})_{11}\text{C}_2\text{N}_8]$  appears to be sufficiently close to the formula of Wohler ( $\text{Ti}_{10}\text{C}_2\text{N}_8$ ) to identify positively the substance examined with his "cyanonitride," yet it is sufficiently different from it to suggest that such a substance does not exist as a definite chemical compound.

A powder X-ray photograph of the sample used for the chemical analyses showed a simple diffraction pattern of the general type produced by sodium chloride. The lines were broad and diffuse, in some cases as wide as  $\frac{3}{4}$  mm, suggesting a mixture of a series of solid solutions in the sample. The best average cell dimension was chosen as  $a = 4.242\text{Å}$  and was obtained from a series of pictures using several different radiations. Table II shows this value as compared with published values of the cell dimensions for related compounds. It is seen to fall between the results determined for TiC and TiN by Hume-Rothery and associates, perhaps the most accurate values, and to lie appreciably nearer the value for titanium nitride. This cell dimension value, combined with the apparent structure ob-

tained from the general diffraction pattern of the powder, indicates strongly that the yellow crystals are primarily a solid solution of one part carbide in 4.7 parts nitride. For additional proof, the space group and structure were determined from a single crystal. The crystal used was a splinter from one of the large but extremely fragile cubes prominent in the sample. It was found to be cubic,  $a = 4.24\text{Å}$ , having  $\text{O}_h^s$  space group. (The single crystal was thus identified with the powdered sample of which the chemical analysis was known.) The intensities of the spots on the zero layer Weissenberg photograph were measured by visual comparison with standard intensity strips. The measured intensities were compared with those calculated for a sodium chloride type structure of titanium nitride and found to check well within the limits of the method of visual measurement. A Fourier projection of the electronic density,  $\rho(x, y)$  was obtained from the measured zero layer structure factors by using Bragg-Huggins masks<sup>5</sup> on a multiple projector. A photograph of the image obtained is shown in Fig. 1a. This shows peaks at all the assumed positions of atoms. It also clearly indicates all spots to be of equal intensity as would be predicted for an end view projection of the assumed structure shown in Fig. 1b. Therefore, it seems apparent that no complex cyanonitride of titanium exists in the yellow crystals found in the iron blast-furnace residues upon cooling.

### Acknowledgments

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Several weeks after completion of the present work, the authors were informed through private communications with Frank Fair, Claude R. Hudgens, and G. L. Clark that some work was then in progress on this subject at the University of Illinois. Upon receiving a preliminary draft of this article, they replied that their results, so far as they had proceeded, checked those obtained by the authors.

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Table I. Results of Chemical Analyses of the Yellow Crystals

| Element  | Percent        | Gram-Atoms |
|----------|----------------|------------|
| Titanium | $71.5 \pm 0.3$ | 1.46       |
| Vanadium | $2.6 \pm 0.1$  | 0.05       |
| Nitrogen | $17.6 \pm 0.2$ | 1.26       |
| Carbon   | $3.3 \pm 0.02$ | 0.27       |
| Total    | 95.0           |            |

Table II. Cell Dimensions of TiC, TiN, and Related Crystals

| Compound        | Lattice Constant (a) | Type Structure | Reported by                                       |
|-----------------|----------------------|----------------|---------------------------------------------------|
| Yellow Crystals | 4.242                | NaCl           | This paper                                        |
| TiC             | 4.320                | NaCl           | Wyckoff <sup>2</sup>                              |
|                 | 4.310                | NaCl           | Dawihl and Rix <sup>3</sup>                       |
|                 | 4.325                | NaCl           | Hofmann, Schraeder, and Hume-Rothery <sup>2</sup> |
| TiN             | 4.22                 | NaCl           | Brager <sup>4</sup>                               |
|                 | 4.23                 | NaCl           | Dawihl and Rix <sup>3</sup>                       |
|                 | 4.233                | NaCl           | Hume-Rothery <sup>2</sup>                         |
| VC              | 4.15                 | NaCl           | Dawihl and Rix <sup>3</sup>                       |
| VN              | 4.13                 | NaCl           | Dawihl and Rix <sup>3</sup>                       |



# Effect of Alloying Elements on True-Stress True-Strain Flow Curves of Pearlitic Steel

by R. Raring, J. A. Rinebolt, and W. J. Harris, Jr.

The effects of additions of alloying elements on the true-stress, true-strain characteristics of 0.30 pct C, 1.00 pct Mn, 0.30 pct Si pearlitic steel were studied. The alloying elements investigated were C, Mn, Si, P, Ni, Cu, V, Mo, Cr, Al, B, S, and Ti. The alloys are compared on the basis of fracture stress, fracture strain, energy to fracture, rate of strain hardening, strain hardening exponent, height of the flow curve, and lower yield point.

IN the past, nearly all studies of the effects of alloying elements on the tensile properties of metals have compared the conventional engineering parameters, namely, tensile strength, yield strength, elongation, and reduction of area. Recently, however, the true-stress, true-strain method of recording results from the tension test has been used; Lacy and Gensamer,<sup>1</sup> Hollomon,<sup>2</sup> and French and Hibbard<sup>3</sup> have used this method to study the effects of composition on strength and ductility of metals. In this paper, the effects of certain alloying elements on true-stress, true-strain curves of steels with nearly constant grain size and pearlite spacing are presented. The notation employed in this paper is given in Table I.

Since the definitions of stress and strain and the analytical geometry of the stress-strain curve have been explained previously, for example by Gensamer,<sup>4</sup> they will not be reviewed here.

However, the method used for the determination of energy to fracture,  $E_f$ , requires mention. These energy values were calculated on the assumption that the flow curve followed the idealized equation:<sup>4</sup>

$$\sigma = \sigma_{0.2} (\delta/0.2)^n$$

and the energy was taken as:

$$E_f = \int_0^{\delta_f} \sigma d\delta = \frac{\sigma_{0.2} \delta_f^{n+1}}{0.2^n (n+1)} \quad [1]$$

This integral was evaluated from  $\delta = 0$  to  $\delta_f$  to obtain the energy absorbed to fracture,  $E_f$ . MacGregor and Fisher have shown<sup>5</sup> that the area under the true-stress, true-strain curve to any strain value

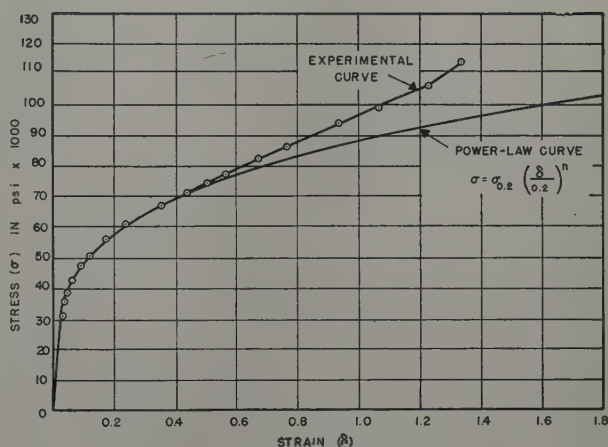


Fig. 1—Experimental stress-strain curve and idealized curve from power law  $\sigma = \sigma_{0.2} (\delta/0.2)^n$ .

corresponds to the specific energy absorption to that strain value.

There is justification for preferring the use of eq 1 for the determination of the energy to a particular strain rather than the area under the experimental stress-strain curve, since Gensamer showed<sup>4</sup> that the use of the Bridgman correction<sup>6</sup> for stress at the neck of a tensile specimen brought the corrected experimental curve nearer to the idealized power-law curve than to the uncorrected experimental curve. However, it should be noted that the difference between the areas under the idealized curve and the experimental curve is not great for strain of less than 1.0, as can be seen from Fig. 1. In this figure, the true-stress, true-strain curve for a 0.01 pct C, 1.00 pct Mn steel is plotted through the experimental data points. From the value of  $\sigma_{0.2}$  from this curve and the value of  $n$  as determined by the  $\ln\sigma$ -

Table I. Nomenclature

|                             |                                                                                     |
|-----------------------------|-------------------------------------------------------------------------------------|
| $\sigma$                    | = true-stress                                                                       |
| $\delta$                    | = true-strain                                                                       |
| $\sigma_t$                  | = true-stress at $\delta = 0$ (extrapolated from the straight portion of the curve) |
| $\sigma_{0.2}$              | = true-stress at $\delta = 0.2$                                                     |
| $\sigma_f$                  | = true-stress at fracture                                                           |
| $n$                         | = slope of the $\ln\sigma$ - $\ln\delta$ plot (strain hardening exponent)           |
| $\delta_f$                  | = true-strain at fracture                                                           |
| $E_f$                       | = energy to fracture                                                                |
| $\Delta\sigma/\Delta\delta$ | = rate of strain hardening                                                          |

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ln $\delta$  plot of the same data, the idealized curve of the power law  $\sigma = \sigma_{0.2} (\delta/0.2)^n$  is also drawn. It can be seen that the experimental curve begins to deviate from the power law at about  $\delta = 0.4$  and the difference between the areas under the two curves to  $\delta = 1.0$  is only about 3 pct. Since most of the steels used in this investigation fractured at strains of less than 1.0, there should not be a great difference between the two areas. It is recognized that the use of the idealized equation for the calculation of  $E_f$  contains an element of inconsistency in that it results, in effect, in an adjustment in  $\sigma_f$  but not  $\delta_f$ . This objection could not be avoided, however, because of the lack of a method of adjusting  $\delta_f$  for the stress state existing at the neck of the specimen.

Material

The steels used in this investigation were made primarily for an investigation of the effects of composition on ductility in the notch-bar impact test; results of these notch-bar tests are reported by Rinebolt and Harris.<sup>7</sup> Since full particulars as to melting, deoxidation, forging, heat-treatment, metallographic and dilatometric techniques, and/or results are contained in ref. 7, they will be but briefly summarized here.

The steels were aluminum-killed; compositions were varied from a base analysis of 0.30 pct C, 1.00 pct Mn, 0.30 pct Si by splitting 250-lb laboratory melts. The final heat treatment was a controlled cooling from 1650° to 800°F at a rate of approximately 25°F per min and then slow cooling from 800°F to room temperature. Dilatometric tests<sup>7</sup>

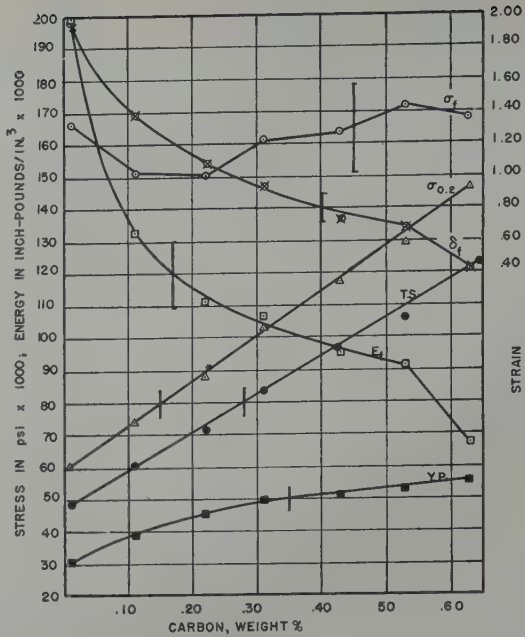


Fig. 2—Variation of strength and ductility parameters with carbon content.

The vertical lines represent the value of four times the standard deviation of the property in 40 tests of 20 different base analysis heats.

showed that this treatment would result in essentially the same difference for all the steels, between the beginning of transformation on heating and the end of transformation on cooling. Since Pellissier,

Table II. Composition and Properties

| Steel | C, Pct | Mn, Pct | Si, Pct | S, Pct | P, Pct | Element Varied | ASTM Ferrite Grain Size | Lower Yield Point, Psi | Elongation, 1.4 In., Pct | Reduction of Area, Pct | $\sigma_t$ , Psi | $\Delta\sigma/\Delta\delta$ Psi per In. per In. | $n$   | $\Delta\sigma/\sigma_t$ |
|-------|--------|---------|---------|--------|--------|----------------|-------------------------|------------------------|--------------------------|------------------------|------------------|-------------------------------------------------|-------|-------------------------|
| C1    | 0.01   | 0.99    | 0.24    | 0.02   | 0.006  | C              | 6                       | 30,000                 | 49.0                     | 86.0                   | 50,000           | 51,400                                          | 0.250 | 1.03                    |
| C2    | 0.11   | 0.99    | 0.24    | 0.02   | 0.010  |                | 8                       | 38,500                 | 47.5                     | 75.0                   | 60,500           | 64,200                                          | 0.218 | 1.06                    |
| C3    | 0.22   | 0.98    | 0.22    | 0.02   | 0.010  |                | 8                       | 45,000                 | 38.5                     | 65.5                   | 72,500           | 74,400                                          | 0.199 | 1.03                    |
| C4    | 0.31   | 1.01    | 0.30    | 0.02   | 0.006  |                | 8                       | 49,500                 | 33.0                     | 60.5                   | 86,000           | 81,000                                          | 0.176 | 0.945                   |
| C5    | 0.43   | 1.02    | 0.28    | 0.02   | 0.006  |                | 8                       | 51,000                 | 28.0                     | 53.0                   | 99,000           | 89,400                                          | 0.160 | 0.905                   |
| C6    | 0.53   | 1.02    | 0.28    | 0.02   | 0.005  |                | 8                       | 52,500                 | 25.5                     | 49.0                   | 109,000          | 95,000                                          | 0.148 | 0.872                   |
| C7    | 0.63   | 0.99    | 0.26    | 0.02   | 0.004  |                | 8                       | 55,000                 | 18.2                     | 34.5                   | 127,500          | 95,400                                          | 0.137 | 0.748                   |
| Mn1   | 0.27   | 0.41    | 0.31    | 0.02   | 0.005  | Mn             | 8                       | 41,500                 | 35.5                     | 59.0                   | 69,500           | 71,700                                          | 0.225 | 1.02                    |
| Mn2   | 0.29   | 0.80    | 0.31    | 0.02   | 0.005  |                | 7                       | 47,500                 | 33.5                     | 59.0                   | 80,000           | 73,600                                          | 0.203 | 0.922                   |
| Mn3   | 0.30   | 1.09    | 0.30    | 0.02   | 0.005  |                | 7                       | 52,000                 | 32.0                     | 61.0                   | 86,000           | 79,400                                          | 0.196 | 0.925                   |
| Mn4   | 0.30   | 1.55    | 0.30    | 0.02   | 0.005  |                | 8                       | 61,000                 | 31.0                     | 67.5                   | 97,000           | 80,000                                          | 0.185 | 0.820                   |
| Si1   | 0.31   | 0.98    | 0.26    | 0.02   | 0.003  | Si             | 8                       | 48,500                 | 34.5                     | 61.0                   | 82,000           | 78,600                                          | 0.217 | 0.960                   |
| Si2   | 0.32   | 0.97    | 1.03    | 0.02   | 0.003  |                | 8                       | 55,000                 | 30.0                     | 57.0                   | 97,500           | 90,600                                          | 0.191 | 0.930                   |
| Si3   | 0.32   | 0.96    | 1.81    | 0.02   | 0.003  |                | 7                       | 62,500                 | 27.0                     | 51.5                   | 108,000          | 94,400                                          | 0.179 | 0.874                   |
| Si4   | 0.33   | 0.98    | 2.52    | 0.02   | 0.004  |                | 7                       | 72,500                 | 25.0                     | 46.0                   | 118,000          | 99,400                                          | 0.160 | 0.842                   |
| Si5   | 0.34   | 0.99    | 3.05    | 0.02   | 0.004  |                | 8                       | 82,000                 | 29.0                     | 46.0                   | 122,000          | 107,600                                         | 0.167 | 0.883                   |
| P1    | 0.29   | 1.00    | 0.30    | 0.02   | 0.005  | P              | 8                       | 51,000                 | 36.5                     | 62.5                   | 82,000           | 78,600                                          | 0.195 | 0.957                   |
| P2    | 0.29   | 1.01    | 0.29    | 0.02   | 0.05   |                | 8                       | 50,000                 | 33.5                     | 59.5                   | 89,000           | 81,000                                          | 0.179 | 0.912                   |
| P3    | 0.28   | 1.01    | 0.28    | 0.02   | 0.12   |                | 8                       | 50,500                 | 33.0                     | 58.5                   | 92,000           | 86,400                                          | 0.172 | 0.940                   |
| P4    | 0.28   | 0.98    | 0.26    | 0.02   | 0.21   |                | 7                       | 58,500                 | 29.5                     | 52.5                   | 98,000           | 90,600                                          | 0.172 | 0.982                   |
| Cu1   | 0.32   | 1.06    | 0.25    | 0.02   | 0.003  | 0.03 Cu        | 8                       | 48,000                 | 31.0                     | 60.0                   | 85,000           | 79,200                                          | 0.204 | 0.933                   |
| Cu2   | 0.32   | 1.04    | 0.27    | 0.02   | 0.003  | 0.50           | 8                       | 54,000                 | 30.5                     | 60.5                   | 88,000           | 84,400                                          | 0.178 | 0.957                   |
| Cu3   | 0.34   | 1.00    | 0.27    | 0.02   | 0.003  | 1.02           | 8                       | 63,500                 | 29.5                     | 57.0                   | 99,000           | 85,200                                          | 0.160 | 0.862                   |
| Cu4   | 0.35   | 1.02    | 0.27    | 0.02   | 0.004  | 1.60           | 8                       | 73,200                 | 25.0                     | 53.0                   | 111,000          | 86,200                                          | 0.151 | 0.779                   |
| Cu5   | 0.34   | 1.01    | 0.27    | 0.02   | 0.004  | 2.00           | 8                       | 79,000                 | 21.5                     | 49.5                   | 118,000          | 89,000                                          | 0.137 | 0.755                   |
| Cr1   | 0.30   | 1.06    | 0.31    | 0.02   | 0.004  | 0.05 Cr        | 7-8                     | 51,500                 | 30.5                     | 62.5                   | 84,500           | 81,000                                          | 0.199 | 0.970                   |
| Cr2   | 0.29   | 1.06    | 0.31    | 0.02   | 0.004  | 0.48           | 8                       | 54,000                 | 29.0                     | 64.0                   | 93,000           | 81,000                                          | 0.174 | 0.882                   |
| Cr3   | 0.29   | 1.03    | 0.29    | 0.02   | 0.004  | 1.10           | 8                       | 55,000                 | 28.5                     | 63.5                   | 96,000           | 84,000                                          | 0.155 | 0.873                   |
| Ni1   | 0.31   | 1.07    | 0.25    | 0.02   | 0.005  | 0.04 Ni        | 7                       | 49,500                 | 35.0                     | 61.5                   | 88,000           | 72,400                                          | 0.184 | 0.823                   |
| Ni2   | 0.30   | 1.06    | 0.25    | 0.02   | 0.005  | 0.40           | 8                       | 54,500                 | 30.0                     | 63.5                   | 84,000           | 79,600                                          | 0.184 | 0.948                   |
| Ni3   | 0.30   | 1.05    | 0.25    | 0.02   | 0.005  | 1.00           | 8                       | 57,500                 | 30.5                     | 65.0                   | 88,000           | 81,800                                          | 0.180 | 0.930                   |
| Ni4   | 0.30   | 1.02    | 0.23    | 0.02   | 0.005  | 1.32           | 8                       | 59,000                 | 34.0                     | 65.5                   | 94,000           | 81,200                                          | 0.163 | 0.865                   |
| Ni5   | 0.29   | 1.01    | 0.22    | 0.02   | 0.006  | 3.15           | 8                       | 65,000                 | 32.0                     | 65.5                   | 101,000          | 86,000                                          | 0.156 | 0.850                   |
| Mo1   | 0.30   | 0.98    | 0.23    | 0.02   | 0.006  | 0.00 Mo        | 8                       | 47,000                 | 35.0                     | 60.0                   | 79,000           | 75,600                                          | 0.179 | 0.958                   |
| Mo2   | 0.29   | 0.98    | 0.21    | 0.02   | 0.11   |                | 8                       | 48,000                 | 34.0                     | 59.0                   | 79,000           | 74,200                                          | 0.179 | 0.940                   |
| Mo3   | 0.29   | 0.94    | 0.19    | 0.02   | 0.18   |                | 7                       | 49,500                 | 33.5                     | 56.5                   | 80,000           | 75,400                                          | 0.179 | 0.943                   |
| Mo4   | 0.29   | 0.90    | 0.15    | 0.02   | 0.29   |                | 7                       | 47,000                 | 30.5                     | 55.0                   | 85,000           | 74,000                                          | 0.173 | 0.872                   |
| V1    | 0.29   | 0.98    | 0.28    | 0.02   | 0.007  | 0.006 V        | 8                       | 49,000                 | 36.0                     | 62.5                   | 81,500           | 78,000                                          | 0.189 | 0.956                   |
| V2    | 0.29   | 0.98    | 0.27    | 0.02   | 0.007  | 0.07           | 7                       | 54,000                 | 31.0                     | 57.5                   | 88,000           | 78,000                                          | 0.165 | 0.886                   |
| V3    | 0.29   | 0.98    | 0.26    | 0.02   | 0.007  | 0.14           | 7                       | 62,500                 | 25.5                     | 55.0                   | 98,000           | 79,800                                          | 0.157 | 0.814                   |
| V4    | 0.29   | 0.93    | 0.22    | 0.02   | 0.007  | 0.21           | 7                       | 65,500                 | 28.0                     | 57.0                   | 95,000           | 82,000                                          | 0.154 | 0.862                   |



Hawkes, Johnson, and Mehl have shown<sup>8</sup> that pearlite spacing is dependent on the difference between the critical temperature and the transformation temperature, all the steels should have very similar pearlite spacing characteristics. No absolute measurements of pearlite spacing were attempted, but several of the lowest and highest alloys of the series were compared by the resolution method<sup>8</sup> and no difference in pearlite spacing could be discerned.

The percentage of pearlite in all alloys was determined with a Hurlbut counter,<sup>9</sup> but no simple relationship between the absolute amount of pearlite and tensile properties was found. No attempts were made to study alloy partition between ferrite and carbide. Ferrite grain size was determined by comparing the structures at X100 with an ASTM grain size chart.

Certain alloy series which appear in the notch-bar impact report<sup>7</sup> were tested in tension, but data from only the Mo series are reported in the present paper because the tensile properties of these series of steels did not differ from those of the base analysis by significant amounts. These series, and the range of the alloying element studied were: Al series—0 to 0.09 pct Al; B series—0 to 0.004 pct B; S series—0.007 to 0.137 pct S; Ti series—0 to 0.39 pct Ti; and Mo series—0 to 0.29 pct Mo.

### Tensile Tests

Threaded-end, 0.357-in. diam tensile specimens with a 1.4-in. gage length were used. An automatic stress-strain recorder was used to measure strains to just beyond the yield point. The strain from the yield point to the fracture point was determined by measuring the minimum diameter of the specimen with pointed micrometers. All tests were made in duplicate and at room temperatures.

The stress-strain data were plotted on Cartesian and on logarithmic coordinates, and the rate of strain hardening,  $\Delta\sigma/\Delta\delta$ , and the value of the strain hardening exponent,  $n$ , were determined from these plots. It was found that the deviation from linear relationship in the logarithmic plot was very slight between the values  $\delta = 0.1$  and  $\delta = 0.3$ ; consequently, the data points in this range of strain were used for the determination of  $n$ .

Results are listed in Table II or presented graphically in Figs. 2 through 10. It can be seen readily that all the alloying elements raised the height of the flow curve.

### Tensile Strength and Lower Yield Point

The tensile strength and the lower yield point were increased by addition of each of the alloying elements studied, not considering Al, B, S, Mo, and Ti. The effects of composition on tensile strength and yield point as reported herein are in close agreement with the results of Kramer, Gorsuch, and Newhouse<sup>10</sup> who investigated steels through much broader composition and cooling rate ranges than are represented by the data of this paper, and therefore will not be discussed further.

### Fracture Stress, Fracture Strain, and Energy to Fracture

The fracture stress,  $\sigma_f$ , and the fracture strain,  $\delta_f$ , are represented by the coordinates of the terminal point of the flow curve, and the energy to fracture,  $E_f$ , is the area under this curve to  $\delta = \delta_f$ ; consequently, it is evident that these values are closely related and can best be considered simultaneously.

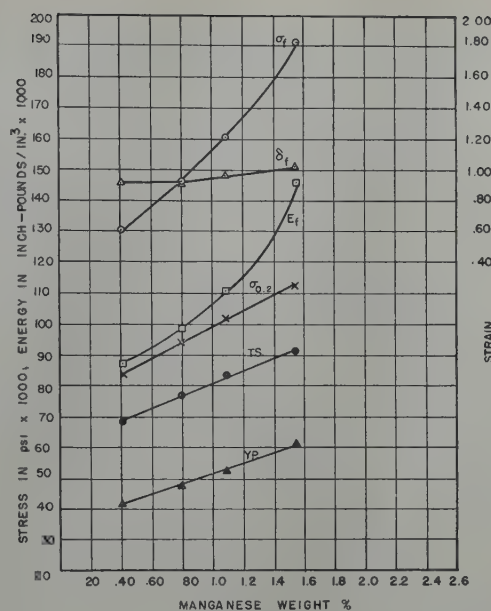


Fig. 3—Variation of strength and ductility parameters with manganese content.

Since the addition of an alloying element increases the height of the flow curve, it follows that: 1—If the addition of an element increases  $\delta_f$ , it must also increase  $\sigma_f$  and  $E_f$ ; 2—if the addition of an alloying element results in no change in  $\delta_f$ , it must cause an increase in  $\sigma_f$  and  $E_f$ ; 3—if the addition of an alloying element results in a decrease in  $\delta_f$ , it can cause either an increase, or a decrease, or no change in the values of  $\sigma_f$  and  $E_f$ , depending upon the degree of the decrease in  $\delta_f$  and the difference in the heights of the flow curves.

In Table III, the qualitative effects of the alloying elements on  $\delta_f$ ,  $\sigma_f$ , and  $E_f$  are listed; the degree of the influence of the various elements on  $\delta_f$ ,  $\sigma_f$ , and  $E_f$  can be seen in Figs. 2 through 10.

The degree of the accuracy realized in the experimental determination of  $\sigma_f$  is likely rather low, and it is considered that much of the scatter in the composition vs.  $\sigma_f$  curves, as shown in Fig. 2, is due to experimental error. This inaccuracy results from

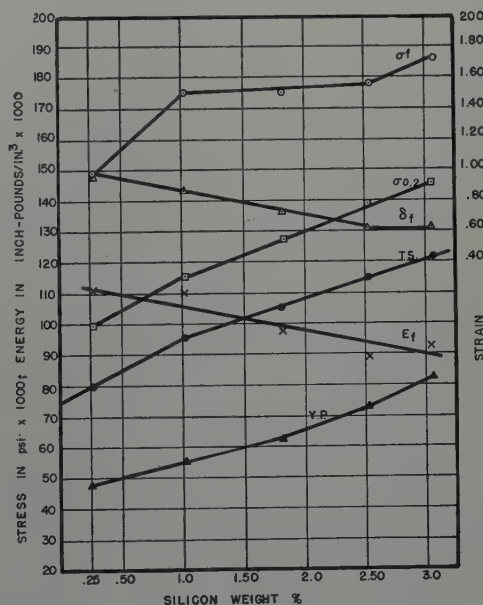


Fig. 4—Variation of strength and ductility parameters with silicon content.

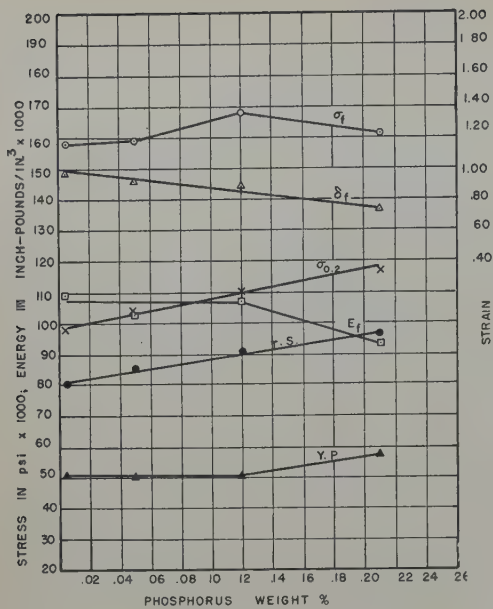


Fig. 5 (left)—Variation of strength and ductility parameters with phosphorus content.

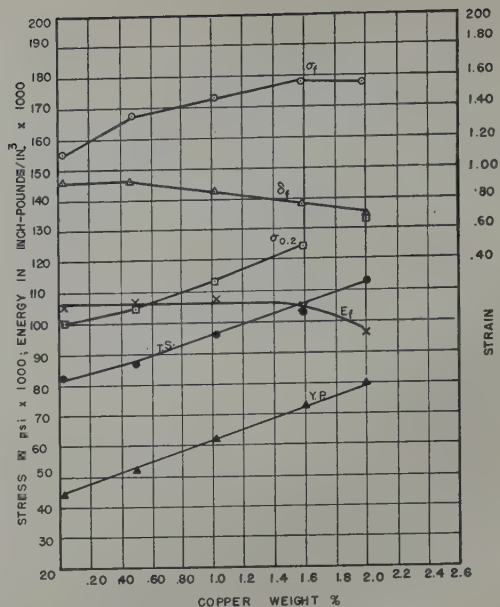


Fig. 6 (right)—Variation of strength and ductility parameters with copper content.

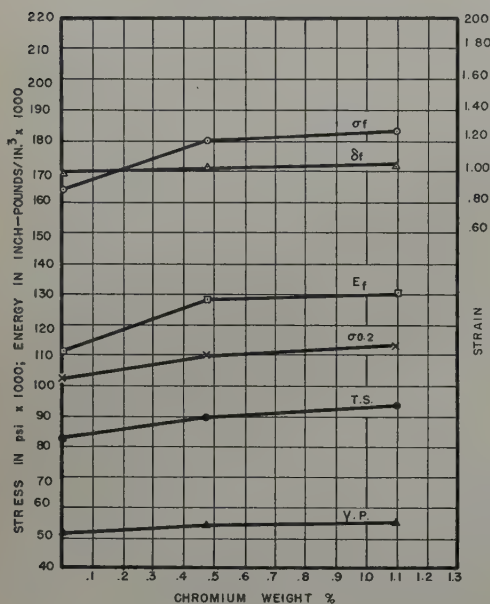


Fig. 7 (left)—Variation of strength and ductility parameters with chromium content.

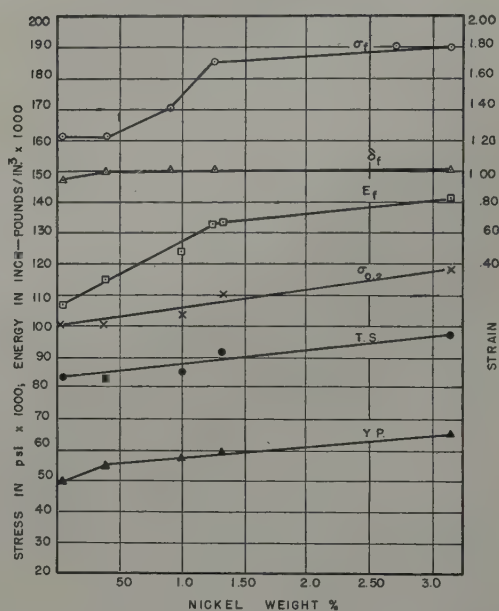


Fig. 8 (right)—Variation of strength and ductility parameters with nickel content.

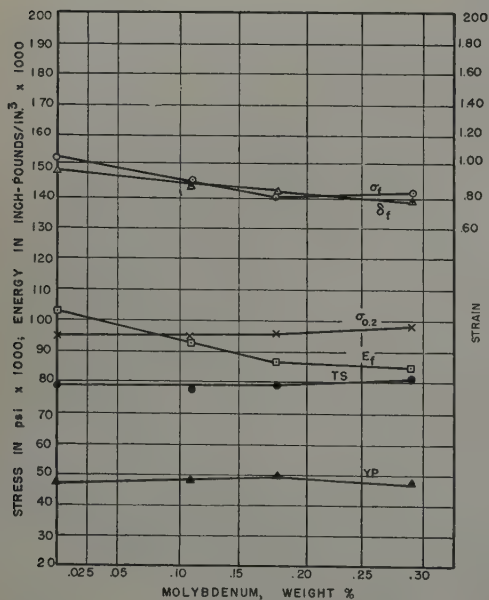


Fig. 9 (left)—Variation of strength and ductility parameters with molybdenum content.

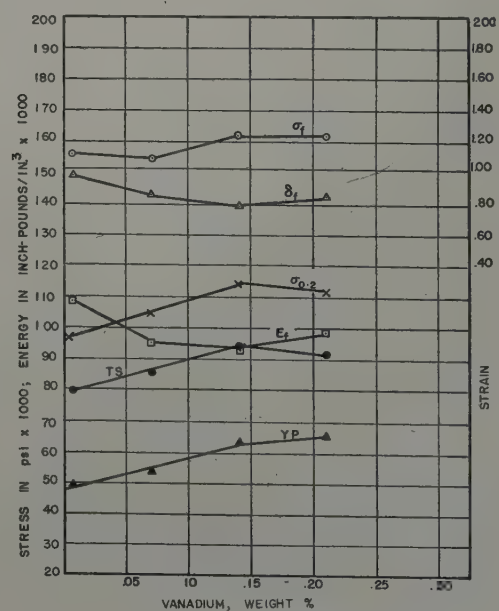


Fig. 10 (right)—Variation of strength and ductility parameters with vanadium content.



the difficulty in reading the load of the tension machine at the instant of fracture of the test bars.

It is considered that the melting and heat-treating practices used eliminated, to the maximum possible extent, variations in such metallurgical factors as inclusions and grain size. The maintenance of uniformity of such factors, which can have an appreciable effect on  $\delta_f$ , is especially important since a change in  $\delta_f$  will result in changes in  $\sigma_f$  and  $E_f$ , and composition effects on  $\delta_f$ ,  $\sigma_f$ , and  $E_f$  could thus be masked. Metallographic checks and the uniformity in properties of the base analysis heats indicated the steels were sufficiently uniform to obviate the possibility that such extraneous factors had appreciable effects.

### Rate of Strain Hardening

The rate of strain hardening,  $\Delta\sigma/\Delta\delta$ , or the slope of the nearly straight portion of the flow curve, was found to increase as the height of the flow curve increased. This relationship is illustrated by Fig. 11, in which the slope is plotted against the intercept at zero strain,  $\sigma_i$ .

Lacy and Gensamer in their studies of alloy ferrites<sup>1</sup> found a linear relationship between slope and  $\sigma_i$ , which would require that the ratio of the slope to the stress at  $\sigma_i$  be a constant. An inspection of the last column of Table II indicates that such a simple relationship does not obtain in the steels used in the investigation. Hollomon,<sup>2</sup> moreover, found that for steels the slope increases with increasing strength differently for different carbon contents.

In Fig. 11, the best lines are drawn for the carbon, the silicon, and the copper series. For comparison, curves of Lacy and Gensamer<sup>1</sup> and of Hollomon<sup>2</sup> representing data on binary ferrites and quenched and tempered carbon steels, respectively, are added to the figure.

Subject to the accuracy of the determination of slope, Fig. 11 indicates that the rate of strain hardening at a given strength level varies with composition. For example, if a given increment of strength is achieved by the addition of Si to the base analysis steel, the rate of strain hardening is increased more than if this same strength increment is realized by adding Cu. A best line drawn through the Mn, P, Cr, or Ni would not be greatly displaced from the Cu or C line; a V line would be about parallel and slightly below the Cu line. It is interesting to note that the binary ferrite data of Lacy and Gensamer fall almost on the carbon line at low carbon levels, and that Hollomon's quenched and tempered 0.20 pct C series indicates that such materials have a much lower rate of strain hardening than pearlitic steels.

### Strain Hardening Exponent

In Fig. 12, the strain hardening exponent,  $n$ , is plotted against intercept at zero strain,  $\sigma_i$ . A

Table IV. Standard Deviations Based on Duplicate Tests of 20 Base Analysis Heats

| Parameter                            | (Standard Deviation)      |
|--------------------------------------|---------------------------|
| Tensile strength                     | 2160 psi                  |
| Yield point                          | 2050 psi                  |
| Fracture stress, $\sigma_f$          | 6680 psi                  |
| Stress at 0.2 strain, $\sigma_{0.2}$ | 2500 psi                  |
| Fracture strain, $\delta_f$          | 0.049                     |
| Strain hardening exponent, $n$       | 0.0113                    |
| Slope, $\Delta\sigma/\Delta\delta$   | 4,214 psi per in. per in. |
| Energy to fracture, $E_f$            | 5,310 in. lb per cu in.   |
| Percent reduction of area            | 1.65 pct                  |
| Percent elongation in 1.4 in.        | 2.82 pct                  |

straight line is drawn through the approximate center of the scatter zone of these data. It is considered that most of the scatter in these data represents experimental error rather than differences in the effects of alloying elements on  $n$ . This error results largely from the necessity of considering only those data within a relatively narrow range of strain values, over which there is very little deviation from the power law, for the establishment of the slope of the  $\ln\sigma$ - $\ln\delta$  plot. For example, if data between  $\delta = 0.15$  and  $\delta = 0.25$  are used for the determination of  $n$  at a strength level which gives a value of  $\sigma_{0.2}$  of approximately 80,000 psi, and if an accuracy of  $\pm 1/2$  pct is assumed in the weighing system of the testing machine, the variation in the determination of  $n$  will be  $\pm 0.01$  due alone to errors in load reading. This error can account for about half of the scatter of the data of Fig. 12. Another possibility of serious error results from the fact that in the range of strain over which  $n$  is determined, the neck is in the initial stages of formation; consequently, the process of locating the minimum diameter of the test bar is difficult and error in the measurement of strain can result. It is interesting, also, to note that the degree of the scatter in the value of  $n$  reported in this paper is approximately of the same order as the scatter reported by Gensamer<sup>4</sup> for steels of various compositions and heat treatments. In view of these possibilities of experimental error in the value of  $n$ , it must be concluded that if there are any effects of the alloying elements studied on the value of  $n$  they are too small to be detected with the present experimental technique.

### Scatter on the True-Stress, True-Strain Test Results

As noted above, a considerable amount of experimental error is to be expected. The reliability of the data and the reality of the trends showing the effects of alloying elements on properties are subject to this error, particularly in those instances in which the total change in the property throughout the series is small. An approximation of the limiting amount of experimental error therefore is considered to be desirable.

The lack of a sufficient number of data from one steel prevented a statistical study of the scatter in one heat. However, it was possible to estimate an upper limit of the scatter by determining the standard deviation in the properties of 20 different heats (the 20 heats were tested in duplicate, thus providing 40 tests) of approximately 0.30 pct C, 1.00 pct Mn, 0.30 pct Si, at least one of which occurred in each series. The maximum variation in composition of these base analysis heats were 0.03 pct C, 0.05 pct Mn, and 0.03 pct Si. These values of standard deviations in properties of the 20 base analysis heats are listed in Table IV.

If it is assumed that the variation in physical

Table III. Effects of Elements on  $\sigma_f$ ,  $\delta_f$ , and  $E_f$

| Alloying Element | Fracture Strain, $\delta_f$ | Fracture Stress, $\sigma_f$ | Energy to Fracture, $E_f$ |
|------------------|-----------------------------|-----------------------------|---------------------------|
| Carbon           | Decreases                   | Constant                    | Decreases                 |
| Manganese        | Increases slightly          | Increases                   | Increases                 |
| Silicon          | Decreases                   | Increases                   | Decreases                 |
| Phosphorus       | Decreases                   | Constant                    | Decreases                 |
| Copper           | Decreases                   | Increases                   | Decreases slightly        |
| Chromium         | Constant                    | Increases                   | Increases                 |
| Nickel           | Constant                    | Increases                   | Increases                 |
| Vanadium         | Decreases                   | Increases                   | Decreases                 |

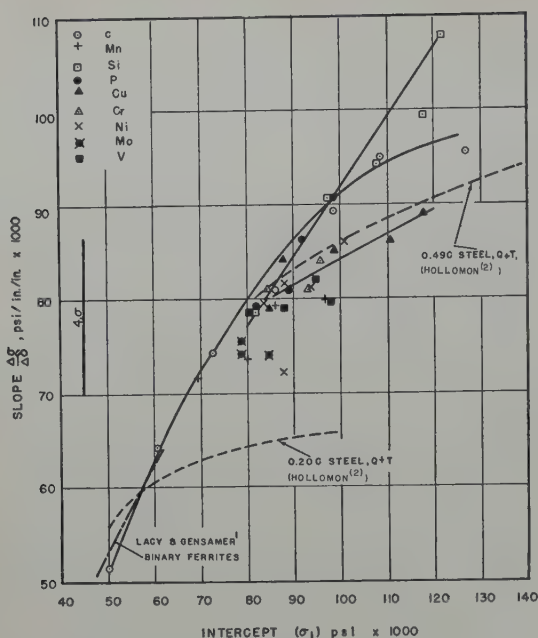


Fig. 11—Variation of the intercept ( $\sigma_i$ ) with rate of strain hardening ( $\Delta\sigma/\Delta\delta$ ).

The vertical line represents the value of four times the standard deviation of slope in 40 tests of 20 different base analysis heats.

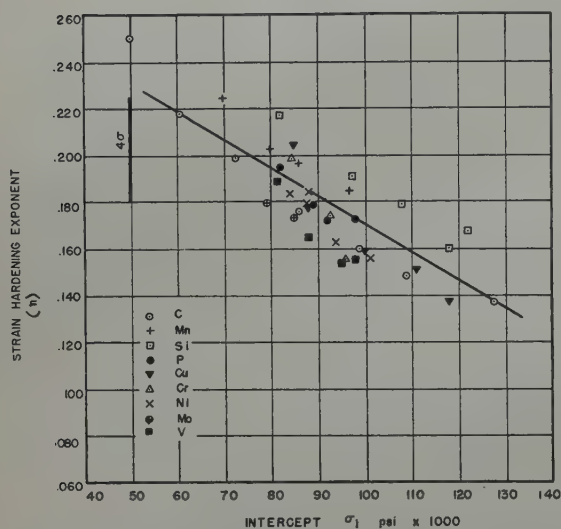


Fig. 12—Variation of intercept ( $\sigma_i$ ) with strain hardening exponent ( $n$ ).

The vertical line represents the value of four times the standard deviation of  $n$  in 40 tests of 20 different base analysis heats.

properties is Gaussian, then the range of plus or minus twice the standard deviation will include 95 pct of the test results. For ready comparison, the value of plus or minus twice the standard deviation ( $\pm 2\sigma$ ) of slope is indicated in Fig. 11, of the strain hardening exponent in Fig. 12, and of  $\sigma_f$ ,  $\delta_f$ ,  $\sigma_{0.2}$ ,  $E_f$ , T.S., and Y.P. in Fig. 2.

In order to demonstrate that the addition of an element changes a given physical property, it would be necessary that the value of the property of the steel without the addition differ from its value with the addition by at least 2.8 times the standard deviation. An inspection of Figs. 2 to 10 will show that this condition is not met in all cases, for ex-

ample, in the Mo series. However, the near-certainty that the standard deviations in properties of the 20 different heats of similar composition would be greater than the standard deviation in single split heats lends credence to the trends in the properties of those series of split heats whose properties changed by less than the 2.8 times the standard deviations shown.

### Summary

1—The effects of C, Mn, Si, P, Cu, Cr, Ni, Mo, V, Al, B, S, and Ti on the true-stress, true-strain curves of pearlitic steels were investigated.

2—All the elements studied except Al, B, S, Mo, and Ti were found to increase the height of the flow curve; effects of Al, B, S, Mo, and Ti were too small to permit reliable evaluation.

3—The rate of strain hardening was found to increase as the height of the flow curve increased; the degree of this increase varied with composition.

4—The strain hardening exponent was found to decrease as the height of the flow curve increased; however, the effects of composition on this relationship, if such effects exist, were too small to be detected by the experimental methods employed.

5—The ratio of the rate of strain hardening to the intercept at zero strain was found to be variable; in this respect the pearlitic steels of this investigation differed from binary ferrites.

6—The energy to fracture was increased by Mn, Ni, and Cr and was decreased by C, Si, P, Mo, Cu, and V.

### Acknowledgment

The authors gratefully acknowledge the encouragement and interest of O. T. Marzke, Superintendent of the Metallurgy Division, and the able assistance of W. S. Kenton and G. G. Gregg, who conducted the tests.

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\* Note the dual use in this paper of the letter "σ" for both stress and standard deviation.



# Thermodynamics of Iron-Silicate Slags: Slags Saturated with Gamma Iron

by R. Schuhmann, Jr. and P. J. Ensio

**As a first step in a study of the physical chemistry of copper-smelting slags, experimental measurements were made of the oxygen pressure of simple iron-silicate slags in equilibrium with solid iron. The experiments consisted in bubbling  $\text{CO}_2$ -CO mixtures through the slags in iron crucibles and in finding the equilibrium ratios of  $\text{CO}_2$  to CO. From the data, activities and partial molal heats of solution FeO and  $\text{SiO}_2$  in the slags were calculated.**

THE ternary system  $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$  is the simplest system which can represent adequately the important chemical properties of the slags formed in matte smelting and converting. Accordingly, the experimental study of slags in this system was started as the first step in a general research program on the thermodynamics of copper smelting. A recent paper by one of the authors<sup>1</sup> outlines this general research program and shows in some detail how information on thermodynamic properties of iron-silicate slags, especially information on oxygen activities, is essential to a full understanding of the chemistry of copper smelting. The  $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$  system also is the basis of slags produced in other processes, such as acid steelmaking processes, and is important in relation to the behavior of silicious refractories. In addition, data on the physicochemical properties of iron-silicate slags should contribute to a general understanding of the nature of slags, since at present such data for all kinds of slags are relatively meager.

The principal quantitative information already available on iron-silicate slags consists in Bowen and Schairer's constitution diagram for slags in equilibrium with metallic iron,<sup>2</sup> Darken and Gurry's complete and precise thermodynamic study of the

Fe-O system,<sup>3,4</sup> and Darken's study of the phase equilibria in the Fe-Si-O system.<sup>5</sup> From the results of this previous work, it was clear that a complete thermodynamic study of ternary iron-silicate melts was a major undertaking which would have to be broken down into parts, including the working out of the ternary equilibrium diagram as well as extensive activity measurements on slags.

The experimental measurement of oxygen activity, using  $\text{CO-CO}_2$  and other gas mixtures as yardsticks of oxygen activity, was the basis of Darken and Gurry's study of the Fe-O system. From the experimental measurements of oxygen activities over a large range of temperatures and compositions, they were able to calculate the activities of other species such as Fe, FeO,  $\text{Fe}_3\text{O}_4$ , etc., and also the other important thermodynamic properties in the Fe-O system. At the start of the present investigation, it appeared that the same approach would be fruitful for the study of iron-silicate melts. Also, the experimental measurement of oxygen activities seemed particularly attractive because oxygen activity itself is a quantitative measure of oxidizing or reducing power, which is an important variable in copper-smelting slags. The slag compositions in equilibrium with  $\gamma$ -Fe appeared most suitable for the first investigation of this kind, for the following reasons: 1—Good constitution data<sup>2</sup> were available. 2—An iron crucible could be used, thus affording a simple solution to the refractory problem without introducing contamination. 3—With Fe activity fixed, at unity with respect to a standard state of solid Fe, measurements of O activity could be followed by simple calculations of activities of FeO and other Fe-O complexes and of  $\text{SiO}_2$ . 4—This starting point afforded several possibilities for cross-checking with previous work,

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This paper is based on a thesis by Mr. Ensio submitted in partial fulfillment of requirements for the degree of Doctor of Science at Massachusetts Institute of Technology.

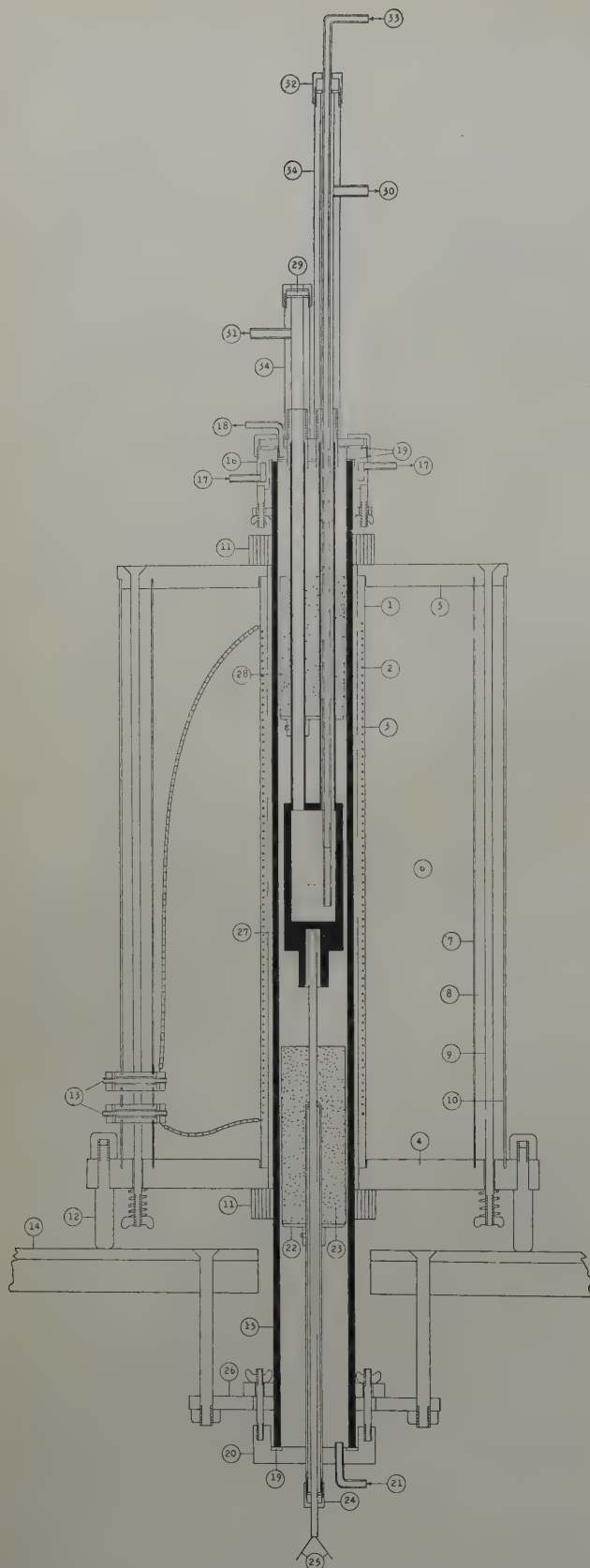


Fig. 1—Resistance furnace, furnace tube, and crucible assembly.

**Platinum-Resistance Furnace:**

- 1—Furnace core
- 2—Resistance element
- 3—Covering on resistance element
- 4—Furnace support plate, 1 in. transite
- 5—Furnace top, 3/4 in. transite
- 6—Insulation
- 7—Inner shell, 1/32 in. carbon steel
- 8—Air space

- 9—Tie rods with expansion springs
- 10—Outer shell, 1/16 in. stainless steel
- 11—Gaskets, 1 in. asbestos tape
- 12—Furnace legs, brass
- 13—Terminals for the electric power
- 14—Table

**Vertical Furnace Tube and Its Accessories:**

- 15—Furnace tube

especially with the work of Darken and Gurry and the work of Bowen and Schairer.

Summarizing, the experimental work reported herein consisted in the determination of  $\text{CO}_2:\text{CO}$  ratios in gas mixtures at equilibrium in the system:

gas:liquid slag: $\gamma$ -iron

Determinations were made over the whole range of slag compositions from wüstite saturation to silica saturation, and at temperatures from  $1250^\circ$  to  $1350^\circ\text{C}$ . Slags were analyzed chemically for  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$ . The composition range covered was 61 to 93 pct  $\text{FeO}$ , 0.5 to 8.5 pct  $\text{Fe}_2\text{O}_3$ , and 0 to 39 pct  $\text{SiO}_2$ . Equilibrium  $\text{CO}_2:\text{CO}$  ratios were determined also at various temperatures for the two univariant systems:

gas:liquid slag: $\gamma$ -iron:wüstite

gas:liquid slag: $\gamma$ -iron:tridymite

From the experimental data relating equilibrium  $\text{CO}_2:\text{CO}$  ratios to slag composition, thermodynamic calculations were made of the activities of  $\text{FeO}$  and  $\text{SiO}_2$  and of the partial molal heats of solution of  $\text{FeO}$  and  $\text{SiO}_2$  in the slags.

### Experimental Methods

The experimental procedure was as follows: A mixture of stock iron-silicate slag with iron oxide or silica was melted in an iron crucible under a  $\text{CO}_2\text{-CO}$  atmosphere and brought to the desired temperature. Then a mixture of  $\text{CO}_2$  and  $\text{CO}$  was bubbled through the melt, and analyses were made of the ingoing gas mixture and of the mixture after bubbling through the melt. The gas composition was adjusted until the analyses of entering and leaving gases became and remained the same, and the  $\text{CO}_2:\text{CO}$  ratio thus finally obtained was considered an equilibrium value. After equilibrium was reached in this way, the melt was sampled and the samples were analyzed for  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$ .

**Furnace and Crucible Assembly:** Fig. 1 shows the complete furnace and crucible assembly. The furnace was a platinum-resistance furnace of essentially standard design built around a vertical aluminum tube of 3-in. bore and 18-in. length. Furnace temperature was controlled automatically by an electronic controller developed by Gordon and Tainton.<sup>9</sup> In this control circuit, the platinum furnace winding is made to be one arm of an ac bridge, and the current through the winding is controlled to maintain the resistance of the platinum winding constant. This arrangement performed well, though requiring occasional expert attention, and maintained constant crucible temperatures within  $\pm 0.5^\circ\text{C}$  for several hours and within  $\pm 2^\circ\text{C}$  for periods of several days.

The crucible assembly was held in a vertical porcelain tube (McDaniel),  $30 \times 2\frac{3}{4}$  in. outside, mounted to extend about 8 in. below and 4 in. above the furnace core. The porcelain tube had water-cooled, brass heads clamped and sealed to

- 16—Gas-tight water-cooled seal
- 17—Cooling water inlet and outlet
- 18—Gas outlet for furnace tube
- 19—Rubber gaskets
- 20—Gas-tight seal
- 21—Gas inlet for furnace tube
- 22—Support for lower radiation shield
- 23—Lower radiation shield
- 24—Gas-tight seal for thermocouple protection tube
- 25—Pt-Pt-Rh thermocouple
- 26—Furnace tube support

**Reaction Chamber Assembly:**

- 27—Iron crucible
- 28—Upper radiation shield
- 29—Removable glass window
- 30—Main gas outlet for reaction chamber
- 31—Alternative gas outlet for reaction chamber
- 32—Gas-tight seal for bubbling tube
- 33—Gas inlet for reaction chamber
- 34—Brass extensions



the tube with rubber gaskets. The upper brass head supported the crucible assembly and was provided with tubes for access to the crucible. The lower brass head carried a tube for admitting gas and an opening through which a thermocouple protection tube was inserted and sealed. Arrangements were made so that either a  $N_2$  or a  $CO_2$ - $CO$  atmosphere could be maintained in the porcelain tube around the crucible, independently of the atmosphere within the crucible.

The crucible assembly is shown more clearly in Fig. 2. The iron crucible, 1½-in. diam and 3¾-in. deep inside, was turned from a cylinder of Armco iron and was provided with a thermocouple well in the bottom. The iron cover was welded to the crucible and the crucible was supported by the two low-carbon steel tubes, ½-in. ID, welded to the cover and extending up into the brass head. Inside one of these tubes was the bubbler tube, made of steel tubing with a 2-in. long replaceable tip made from Armco iron. The bubbler tube could be moved up or down through a gas-tight seal in the head, so that it could be raised out of the slag if desired. The main path of gas flow through the crucible assembly was in the bubbler tube, through the slag and crucible, and then out in the annular space between the bubbler tube and the larger steel tube around the bubbler tube. The other ½-in. steel tube provided access to the crucible for sampling, adding materials, observation, etc. Normally it was closed with a sight glass clamped and rubber sealed to the top opening of the access tube, as shown in Fig. 1. The whole crucible assembly was made as compact and gas tight as possible, so that the gas composition inside could be controlled independently of that in the surrounding furnace tube. In this way a system was obtained for which the outlet gas composition would respond quickly and fully to changes in the reacting phases. Such response, of course, greatly facilitated the location of equilibrium by the method of comparing ingoing and outgoing gas analyses.

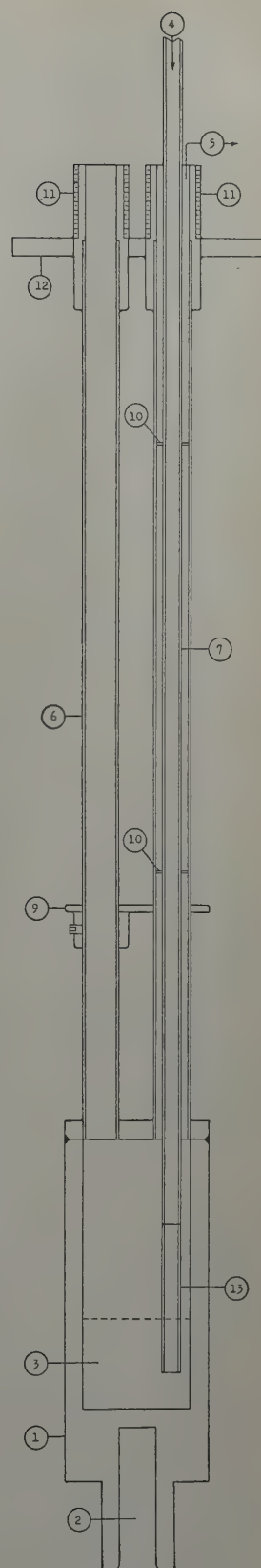
The average charge for an equilibrium run was around 150 g of slag, which in the molten state filled the crucible to a depth of under 50 mm. The gas mixture was passed through the slag at the rate of about 100 ml per min.

**Temperature Measurement:** Temperatures were measured with Pt—Pt-Rh thermocouples calibrated at the melting point of gold. The thermocouple, in a porcelain protection tube, was inserted up through the bottom of the furnace tube into the well on the crucible bottom and left in position during each run.

Before the equilibrium runs were made, the temperature distribution in the empty crucible was investigated in some detail. Readings of couples inserted in porcelain protection tubes through the access tube to various levels in the crucible were compared to readings obtained simultaneously with another couple in the well on the crucible bottom. Inside the crucible from the bottom upwards the temperature decreased about 0.2°C in the first 25 mm and then decreased further about 3°C in the next 25 mm, so that the slag was in a zone in which the temperature was probably uniform within about 3°C. The temperature dropped more sharply in the upper part of the crucible, readings with the junction just at the crucible lid falling about 20°C below those near the bottom. The couple inserted from below into the well gave readings from 10° to 16°C below those obtained inside the crucible

Fig. 2—Crucible assembly.

- 1—Iron crucible
- 2—Thermocouple well
- 3—Molten slag
- 4—Incoming gas
- 5—Outgoing gas
- 6—Charging and sampling tube, low carbon steel tubing, ½ in. ID, 1/32 in. wall
- 7—Adjustable gas inlet tube, ¼ in. OD, 1/32 in. wall
- 8—Gas outlet tube, ½ in. ID, 1/32 in. wall
- 9—Support for upper radiation shield
- 10—Spider
- 11—Threads for extension tubes
- 12—Plate supporting reaction chamber
- 13—Armco iron tip



near the bottom, and the temperature gradient in the well appeared to be steeper than in the crucible. In view of these characteristics, the thermocouple in the well, with which all final temperature measurements were made, was calibrated against a couple inside the crucible with the furnace at temperature but before adding slag for each run. The correction thus measured was applied to all read-

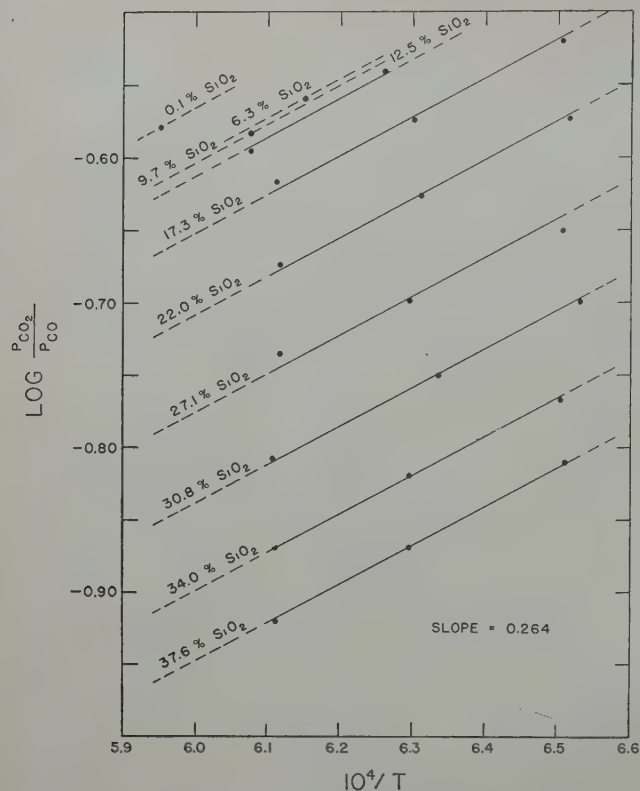


Fig. 3—Log  $p_{CO_2}/p_{CO}$  vs.  $10^4/T$  for equilibria with Fe-saturated slags of varying  $SiO_2$  content.

ings made during the run. This correction was checked several times by comparing the corrected temperature with the reading of a couple in a porcelain or silica protection tube, with a thin iron sheath on the lower end to prevent attack by the slag, actually immersed in the slag. Difficulties in maintaining protection tubes inside the crucible prevented the more extensive use of immersed couples.

On the basis of the temperature-distribution measurements outlined above, the temperatures reported in the experimental data are thought to represent actual slag temperatures to  $\pm 3^\circ C$ .

**Preparation of  $CO_2$ -CO Mixtures:** The gas mixtures, consisting of purified  $CO_2$  and CO at a total pressure of substantially 1 atm, were prepared by essentially the same procedure as that described by Darken and Gurry<sup>9</sup> using flowmeters with pressure bleeders up and downstream to maintain automatically a constant gas composition. No difficulty was experienced in holding the gas composition constant to well within 0.1 pct  $CO_2$  for long periods.

The gas trains were of all-glass construction, except for short rubber connections at the main furnace, the  $CO_2$  tank, and the furnace in which  $CO_2$  was reduced to CO with graphite.

**Gas Analyses:** Two methods of analyzing the incoming and outgoing gas mixtures were used. During the period of adjustment of the gas composition, the outgoing gas was continuously analyzed and the analysis was recorded by means of a Leeds and Northrup thermal-conductivity unit and Micro-max recorder. This automatic and quick gas analysis saved a large amount of time and analytical labor and is strongly recommended for studies in which comparison of ingoing and outgoing gas analyses is used as a criterion of equilibrium. After the thermal-conductivity analysis indicated the in-

going and outgoing gas compositions to be the same to  $\pm 0.2$  pct  $CO_2$ , final adjustments and determinations of equilibrium  $CO_2$ :CO ratios were made with chemical analyses of the gases.

The chemical procedure of gas analysis was as follows: First the  $CO_2$  was absorbed in a train of ascarite and anhydron, then the CO was oxidized to  $CO_2$  in a copper-oxide combustion furnace, and finally the  $CO_2$  formed from CO was absorbed in a second train of ascarite and anhydron. Purified nitrogen was used for flushing the whole analytical train before and at the end of each analysis. By this procedure, both  $CO_2$  and CO were measured as weights of  $CO_2$ , and the weight ratio was considered to be the ratio of partial pressures, assuming ideal gas behavior. For the gas mixtures from 10 to 25 pct  $CO_2$  (balance CO) used in this investigation, the analyses were readily reproducible to  $\pm 0.05$  pct  $CO_2$ .

**Sampling and Analyses of Slags:** After equilibrium was established, the slag was sampled by inserting a long,  $1/4$ -in. diam, Armco-iron rod into the molten slag for a few seconds. The hot sample of 1 to 4 g then was lifted up into the cold part of the furnace and allowed to cool in contact with the  $CO_2$ -CO furnace atmosphere. Normally three to five duplicate samples were taken from each equilibrium slag and stored immediately in closed glass bottles.

Three determinations, namely silica, total iron, and ferric iron, were made to determine the slag composition. The first two determinations were straight-forward and could be carried out by standard methods to an accuracy of 0.1 pct. However, some difficulties were experienced in obtaining reliable and reproducible analyses for ferric iron. The method finally adopted consisted in dissolving a slag sample in HCl under a  $CO_2$  atmosphere and then titrating with  $TiCl_3$ , using  $NH_4SCN$  as indicator and maintaining the  $CO_2$  atmosphere at all steps. Part of the difficulty in obtaining reproducible results was traced to oxidation of the samples during grinding in the agate mortar, so that finally the samples were ground quickly only to -20-mesh. A longer time was required for bringing these coarse samples into solution.

The results of the slag analyses, calculated to pct FeO, pct  $Fe_2O_3$ , and pct  $SiO_2$ , added up to between 99.25 and 100.0 total pct in all cases and to between 99.6 and 100.0 pct in the majority of samples. Accordingly, the percentages of FeO,  $Fe_2O_3$ , and  $SiO_2$  were corrected slightly to add up to 100 pct exactly, and are so reported in the experimental data.

**Materials:** The stock fayalite slag was prepared in a large Armco-iron crucible from Baker cp ferric oxide, Mallinckrodt hydrogen-reduced iron powder,

Table I. Effect of Side Reactions on the Composition of Gas Passing Through the Empty Reaction Chamber at  $1250^\circ C$

| Time After Starting, Hr | Gas — 1          |                   | Gas — 2          |                   | Gas — 3          |                   |
|-------------------------|------------------|-------------------|------------------|-------------------|------------------|-------------------|
|                         | In, $CO_2$ , Pct | Out, $CO_2$ , Pct | In, $CO_2$ , Pct | Out, $CO_2$ , Pct | In, $CO_2$ , Pct | Out, $CO_2$ , Pct |
| 0                       | 18.43            |                   |                  |                   |                  |                   |
| 1                       | 18.51            | 18.50             |                  |                   |                  |                   |
| 2                       | 18.45            | 18.53             | 12.41            |                   |                  |                   |
| 3                       |                  |                   | 12.41            | 13.28             |                  |                   |
| 4                       |                  |                   | 12.41            | 13.11             |                  |                   |
| 5                       |                  |                   | 12.41            | 12.90             |                  |                   |
| 6                       |                  |                   | 12.44            | 12.66             | 7.61             |                   |
| 7                       |                  |                   |                  |                   | 7.61             | 8.57              |
| 8                       |                  |                   |                  |                   | 7.61             | 8.47              |
| 9                       |                  |                   |                  |                   | 7.67             | 8.32              |



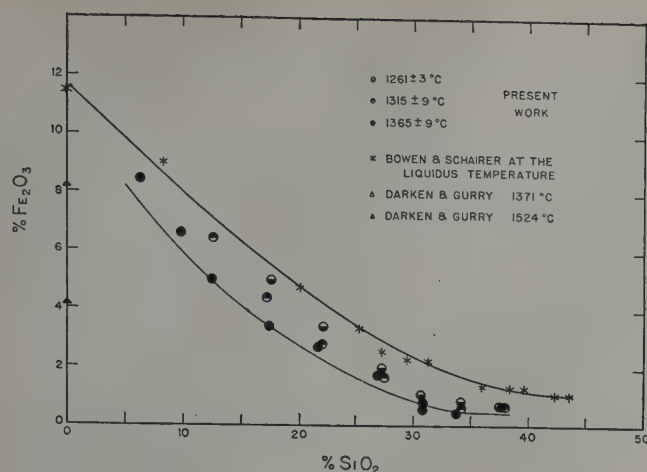


Fig. 4— $\text{Fe}_2\text{O}_3$  contents of iron-silicate slags in equilibrium with solid iron.

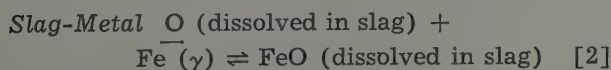
and precipitated silica. A mixture calculated to yield a slag corresponding to fayalite ( $2\text{FeO} \cdot \text{SiO}_2$ ) in composition was heated at  $1350^\circ$  to  $1400^\circ\text{C}$  for complete fusion. The temperature was then lowered to  $1300^\circ\text{C}$  and the molten slag was kept at that temperature for 1 hr to let it become homogeneous and approach equilibrium with the iron crucible. The slag was then cast into an iron mold, cooled, crushed, and screened. The fraction  $-6 + 20$ -mesh was used for the stock. Chemical analysis gave 67.3 pct FeO, 4.1 pct  $\text{Fe}_2\text{O}_3$  and 28.4 pct  $\text{SiO}_2$ .

The iron oxide was prepared by oxidizing a bar of Armco iron in an electric furnace at  $1200^\circ\text{C}$ , collecting the scale, and screening. The fraction  $-6 + 20$ -mesh was again used for making up the slags and was found to analyze 71.2 pct FeO, 28.5 pct  $\text{Fe}_2\text{O}_3$ .

The silica was prepared from silica glass (99.8 pct  $\text{SiO}_2$ ) by crushing and then screening out the desired  $-6 + 20$ -mesh fraction.

### Chemical Reactions and Establishment of Equilibrium

The principal reactions for which equilibrium must be established are those between the gas and the slag and between the iron crucible and the slag, which can be written:



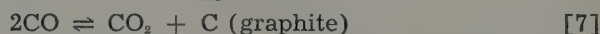
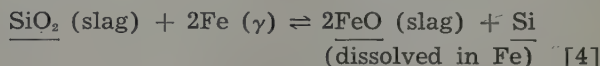
Reaction 1 was found to be quite rapid when a gas mixture was bubbled through liquid slags under the conditions of the present work. In fact for low-silica slags, the gas leaving the melt generally had a  $\text{CO}_2:\text{CO}$  ratio close to that corresponding to equilibrium with the slag, regardless of the  $\text{CO}_2:\text{CO}$  ratio in the gas brought in through the bubbler tube. For high-silica slags the reaction was slower, but still rapid enough that there was no difficulty in detecting the direction of reaction by comparison of ingoing and outgoing gas analyses. In addition to the high reaction rates afforded by the intimate gas-liquid contact, the bubbling method furnished good agitation of the slag and also eliminated the possibility of errors due to thermal diffusion. Accordingly, the very satisfactory experience in the present work with the procedure of bubbling the gas through the melt has led to the adoption of the

same technique in other high-temperature, gas-liquid equilibrium studies in this laboratory.

Bowen and Schairer found that equilibrium in reaction 2 was quickly reached between iron crucibles and iron silicate slags. Slow attainment of equilibrium in this reaction in the present work would have caused a drift in the measured  $\text{CO}_2:\text{CO}$  equilibrium ratios, and such a drift never was found. Moreover, by the time the final equilibrium was established for each slag, the slag had been at constant temperature and at substantially constant composition in the iron crucible for several hours.

Theoretically, there are two possible procedures for finding the equilibrium gas and slag compositions: 1—Bring a given slag mixture to equilibrium with solid iron and then vary the gas composition until the equilibrium  $\text{CO}_2:\text{CO}$  ratio is found. 2—Fix the gas composition, the  $\text{CO}_2:\text{CO}$  ratio, and allow reactions 1 and 2 to occur until the slag reaches a composition in equilibrium with the gas. Simple stoichiometric calculations show that the second procedure would be very time-consuming, so the first procedure was used throughout the work. The stoichiometric calculations also showed the impracticality of using rate of change of slag analysis as a criterion of equilibrium.

**Secondary Reactions:** Other reactions which could be expected in the gas-slag-metal system are the following:



Reactions 3, 4, and 5 undoubtedly occurred, but quantity estimates based on known equilibrium data for these reactions indicated their effects on the experimental results would be negligible. On the

Table II. Gas-Solid Iron-Liquid Slag Equilibria, Experimental Data

| Run No. | Temperature, °C | Chemical Analysis of Slag,* Pct |                         |       | Ratio $\text{pCO}_2:\text{pCO}$ |
|---------|-----------------|---------------------------------|-------------------------|-------|---------------------------------|
|         |                 | $\text{SiO}_2$                  | $\text{Fe}_2\text{O}_3$ | FeO   |                                 |
| 1       | 1263            | 37.4                            | 0.7                     | 61.9  | 0.155                           |
| 2       | 1315            | 37.6                            | 0.7                     | 61.7  | 0.135                           |
| 3       | 1364            | 37.9                            | 0.7                     | 61.4  | 0.120                           |
| 4       | 1264            | 34.1                            | 0.85                    | 65.05 | 0.171                           |
| 5       | 1315            | 34.0                            | 0.6                     | 65.4  | 0.1515                          |
| 6       | 1364            | 33.85                           | 0.45                    | 65.7  | 0.135                           |
| 7       | 1258            | 30.7                            | 1.05                    | 68.25 | 0.200                           |
| 8       | 1305            | 30.8                            | 0.8                     | 68.4  | 0.178                           |
| 9       | 1365            | 30.9                            | 0.65                    | 68.45 | 0.1555                          |
| 10      | 1264            | 27.2                            | 1.95                    | 70.85 | 0.224                           |
| 11      | 1315            | 27.1                            | 1.7                     | 71.2  | 0.2005                          |
| 12      | 1362            | 27.05                           | 1.75                    | 71.2  | 0.1845                          |
| 13      | 1262            | 22.2                            | 3.4                     | 74.4  | 0.2765                          |
| 14      | 1312            | 21.9                            | 2.8                     | 75.3  | 0.2365                          |
| 15      | 1362            | 21.95                           | 2.75                    | 75.3  | 0.2125                          |
| 16      | 1264            | 17.5                            | 4.95                    | 77.55 | 0.3025                          |
| 17      | 1314            | 17.15                           | 4.4                     | 78.45 | 0.2675                          |
| 18      | 1364            | 17.3                            | 3.4                     | 79.3  | 0.2415                          |
| 19      | 1324            | 12.5                            | 6.4                     | 81.1  | 0.288                           |
| 20      | 1374            | 12.45                           | 5.0                     | 82.55 | 0.254                           |
| 21      | 1374            | 9.75                            | 6.6                     | 83.65 | 0.261                           |
| 22      | 1356            | 6.3                             | 8.45                    | 85.25 | 0.276                           |
| 23      | 1407            | 0.1                             | 7.15                    | 92.75 | 0.2635                          |

\* Average values from duplicate analyses corrected to 100 pct.

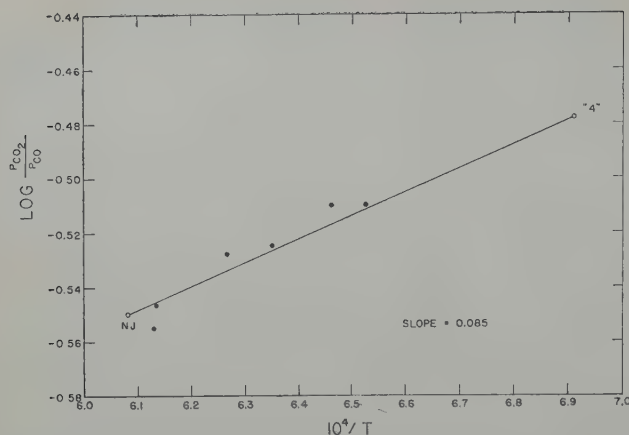


Fig. 5—Log  $p_{CO_2}/p_{CO}$  vs.  $10^4/T$  for equilibria with slag:wüstite: $\gamma$ -iron.

Results of present work are given by black circles; the straight line and the points of invariant equilibria NJ are based on work of Darken and Gurry.

other hand, it appeared that the effects of reactions 6 and 7 could not be ignored. That is, approximately equal reaction rates to the right in reaction 1 and in either reaction 6 or 7 would result in no net change in gas composition through the system, thus giving a false indication of equilibrium in reaction 1.

Reaction 6 has been studied recently by Smith.<sup>7</sup> Smith's work showed that at temperatures of 1150° to 1350°C, the gas mixtures used in the present investigation, namely 10 to 25 pct  $CO_2$ , balance  $CO$ , would be decarburizing to Armco iron; that is, reaction 6 would tend to go to the left and only a small total amount of C could be involved in reaching equilibrium, starting with a new crucible. However, at lower temperatures in the steel tubes through which the gas enters and leaves the crucible a zone of conditions most favorable to carburization of the iron is to be expected. Similarly, equilibrium data for reaction 7 show no possibility of graphite formation in the crucible and high-temperature zone of the system. However, when both equilibrium and reaction rate information on this reaction are considered, again a zone at intermediate temperature most favorable to C deposition is to be expected in the steel tubes above the crucible. Such a zone was readily observed, especially with gases of 90 pct or more  $CO$ .

The effects of the side reactions of carburization and C deposition were studied by making a blank run at 1250°C on a new, empty crucible assembly. Data for this run, given in Table I, indicate that these reactions had little effect on gas composition for gases containing 12 pct or more  $CO_2$  but had a serious effect for gases lower in  $CO_2$ .

To minimize the effects of the side reactions, the following procedure was adopted for the gas-slag equilibrium runs. When it appeared that the gas composition was adjusted substantially to equilibrium with the slag, the bubbler tube was raised out of the melt so that the gas merely passed over the melt and then out to the analytical train. Raising the bubbler tube should reduce the rate of the gas-slag reaction without affecting the rates of the side reactions. Accordingly, when gas-slag equilibrium is reached, the analysis of the outgoing gas should be the same with the bubbler up or down, although the outgoing gas might be higher in  $CO_2$  than the incoming gas because of the side reactions. Most of the runs were continued until the  $CO_2$  percentages in the incoming gas, the outgoing gas with

bubbling, and the outgoing gas without bubbling agreed within 0.2 pct, but in a few cases such close agreement was not reached even after rather long runs.

## Experimental Results

In all, 33 equilibrium runs were made, the duration of the runs from start of bubbling at temperature to the end averaging about 7 hr each. Of these 33 runs, 23 were on slags of varying silica content at temperatures ranging from 1250° to 1400°C, seven were on wüstite-saturated slags at temperatures from 1250° to 1350°C, and three were on silica-saturated slags at temperatures from 1250° to 1350°C.

Table II gives the data on gas-slag-iron equilibrium for slags of varying silica content. In Fig. 3 is given a plot of  $\log p_{CO_2}/p_{CO}$  against  $10^4/T$  from the same data. For slags of given  $SiO_2$  content, it can be seen that the points are fitted by straight lines within the experimental error. All the lines in Fig. 3 are drawn with a slope of 0.264, even though slightly different slopes would result if each line were drawn independently with best fit to the three experimental points. The reasons for presenting the data in this way are discussed later. However, it should be pointed out that the largest deviations from the lines, obtained with the data for 27.1 pct  $SiO_2$ , correspond to an error of only 0.3 pct  $CO_2$  in the gas analysis or only 10°C in the temperature.

Fig. 4 shows the variation of equilibrium pct  $Fe_2O_3$  with pct  $SiO_2$  for the slags in iron crucibles at various temperatures. Also shown are the previous results of Bowen and Shairer at liquidus temperatures and the recommended values of Darken and Gurry for 0 pct  $SiO_2$  slags. The results are not as concordant as might be desired, probably owing to difficulties in making accurate analyses for  $Fe_2O_3$ . However, certain trends are evident. First, the equilibrium pct  $Fe_2O_3$  clearly decreases with increasing pct  $SiO_2$ , and the present results are in semiquantitative agreement on this score with the findings of Bowen and Schairer. Second, for slags of fixed pct  $SiO_2$  in Fe crucibles, the equilibrium pct  $Fe_2O_3$  decreases very slowly with increasing temperature and appears least affected by temperature at high pct  $SiO_2$ . Bowen and Schairer concluded that the effect of temperature on pct  $Fe_2O_3$  in the Fe-saturated silicate melts was too small to be detected by their analytical methods. Similarly, Darken and Gurry's experimental results on Fe-saturated melts at 0 pct  $SiO_2$  were too scattered to furnish a good direct measure of this change, but their recommended constitution diagram for the

Table III. Gas-Solid Iron-Wüstite-Liquid Slag Equilibria, Experimental Data

| Run No. | Temperature, °C | Slag Composition by Analysis,* Pct |           |       | Gas Composition by Analysis |
|---------|-----------------|------------------------------------|-----------|-------|-----------------------------|
|         |                 | $SiO_2$                            | $Fe_2O_3$ | FeO   | Ratio $p_{CO_2}:p_{CO}$     |
| 24      | 1259            | 12.7                               | 7.1       | 80.2  | 0.309                       |
| 25      | 1302            | 6.3                                | 8.45      | 85.25 | 0.299                       |
| 26      | 1323            | 9.75                               | 6.6       | 83.65 | 0.296                       |
| 27      | 1275            | 15.8                               | 5.35      | 78.85 | 0.309                       |
| 28      | 1306            | 10.3                               | 7.7       | 82.0  | 0.299                       |
| 29      | 1357            | 3.65                               | 9.6       | 86.75 | 0.284                       |
| 30      | 1358            | 3.1                                | 8.6       | 88.3  | 0.279                       |

\* Average values from duplicate analyses corrected to 100 pct. In Runs 24-26 analyses were on samples taken from the homogeneous melt at about 50°C above the final equilibrium temperature. In Runs 27-30 analyses are on samples of the saturated slag at the equilibrium temperature.



Fe-O system shows a decrease of 2.6 pct Fe<sub>2</sub>O<sub>3</sub> per 100°C increase in temperature.

Table III gives the results obtained in equilibrium measurements on slags saturated both with wüstite and with solid iron. The procedure used in these runs was as follows: The high-FeO slags were melted and held for 2 hr at 1350°C to insure homogeneity and equilibrium with the crucible. Then the system was cooled and brought to thermal equilibrium at a temperature for which, according to Bowen and Schairer's constitution diagram, substantial precipitation of wüstite should occur. The equilibrium CO<sub>2</sub>:CO ratio was determined by the usual procedure. Then, stock slag was added to the crucible to increase the SiO<sub>2</sub> content by 2 or 3 pct and the equilibrium CO<sub>2</sub>:CO ratio again determined. A check of the two CO<sub>2</sub>:CO ratios for different SiO<sub>2</sub> percentages in the mixture was taken as evidence of wüstite saturation.

A plot of log CO<sub>2</sub>/CO against 10<sup>4</sup>/T for the gas-slag-iron-wüstite equilibria is given in Fig. 5. The straight line is represented by the equation:

$$\log \frac{p_{CO_2}}{p_{CO}} = \frac{850}{T} - 1.068 \quad [8]$$

and is based on the data for the gas-iron-wüstite equilibria recommended by Darken and Gurry<sup>3</sup> on the basis of their own experimental work as well as the earlier work of Chipman and Marshall,<sup>8</sup> Emmett and Schultz,<sup>9,10</sup> and Schenck and coworkers.<sup>11</sup> The lower temperature terminus of the line (Darken's<sup>5</sup> invariant point 4) is at the temperature at which the slag is in equilibrium with γ-Fe, wüstite, and fayalite; the higher temperature terminus (point NJ) is at the melting point of wüstite. The results of the present work, with slag as an additional phase and silica as an additional component, clearly confirm the results of the previous work. The maximum deviation of the new data from the relation recommended by Darken and Gurry corresponds to a difference of only 0.4 pct CO<sub>2</sub> in the analysis of the CO-CO<sub>2</sub> mixture.

Table IV gives the results obtained on slags saturated with silica and with solid iron. For these runs a slag mixture estimated to be just under saturation with SiO<sub>2</sub> was charged into the iron crucible and fused at 1400°C. A rod of silica glass was inserted into the melt and left for several hours, with occasional removal for inspection. The rod was attacked strongly at the start, but after 6 hr no further attack was noticeable. A sample of the slag at this stage analyzed 39.7 pct SiO<sub>2</sub>, in good agreement with expectations from Bowen and Schairer's

Table IV. Gas-Solid Iron-Solid Silica-Liquid Slag Equilibria, Experimental Data

| Run No. | Temperature, °C | Slag Composition by Analysis,* Pct |                                |      | Gas Composition by Analysis<br>Ratio p <sub>CO2</sub> :p <sub>CO</sub> |
|---------|-----------------|------------------------------------|--------------------------------|------|------------------------------------------------------------------------|
|         |                 | SiO <sub>2</sub>                   | Fe <sub>2</sub> O <sub>3</sub> | FeO  |                                                                        |
| 31      | 1260            | 39.7                               | 0.5                            | 59.8 | 0.148                                                                  |
| 32      | 1310            | 39.7                               | 0.5                            | 59.8 | 0.132                                                                  |
| 33      | 1352            | 39.7                               | 0.5                            | 59.8 | 0.116                                                                  |
| X**     | 1180            | 38.0                               | 1.3                            | 60.7 | 0.189                                                                  |

\* Average values from duplicate analyses corrected to 100 pct. Analyses are on samples taken from the homogeneous melt at about 50°C above the final equilibrium temperature.  
\*\* Darken's value for the CO<sub>2</sub>:CO ratio at the quintuple point in which iron, silica, fayalite, and slag are all present at equilibrium. Bowen and Schairer's values for temperature and composition.

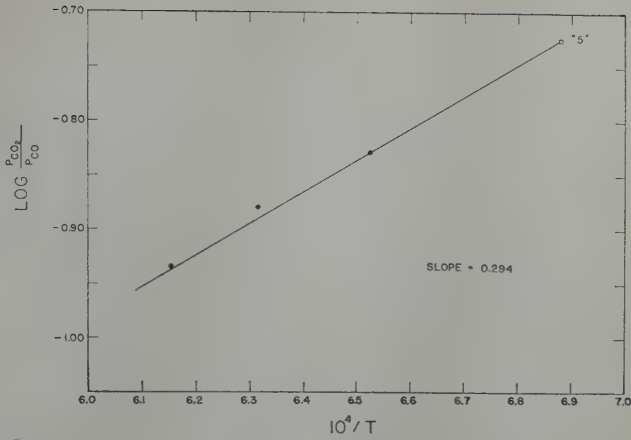


Fig. 6—Log p<sub>CO2</sub>/p<sub>CO</sub> vs. 10<sup>4</sup>/T for equilibria with slag:silica:γ-iron. Results of present work are given by black circles; invariant point 5 is taken from Darken.

data. After it appeared that silica saturation at 1400°C had been attained in this way, the temperature was successively lowered for the determinations of equilibrium CO<sub>2</sub>:CO ratios at 1352°, 1310°, and 1260°C. Table IV also includes data taken from previous work for the invariant point at which slag, iron, silica, and fayalite are in equilibrium.

Fig. 6 shows the relation between log p<sub>CO2</sub>/p<sub>CO</sub> and 10<sup>4</sup>/T for the SiO<sub>2</sub>-saturated slags. The straight line was drawn from the invariant point 5, giving most weight to the experimental point at lowest temperature, and follows the equation:

$$\log \frac{p_{CO_2}}{p_{CO}} = \frac{2940}{T} - 2.747 \quad [9]$$

A diagram summarizing the now available information on the relation of log p<sub>CO2</sub>/p<sub>CO</sub> to 10<sup>4</sup>/T for the entire range of stability of iron-silicate slags in contact with solid iron is given in Fig. 7. This range of stability is shown by the closed area C-NJ-4-5-D, and the boundary lines and curves correspond to the following limiting conditions:

- Line NJ-4: Wüstite saturation
- Curve 4-5: Fayalite saturation
- Line 5-D: Silica saturation
- Line D-C: Melting point of iron
- Line C-NJ: Slags of 0 pct SiO<sub>2</sub>

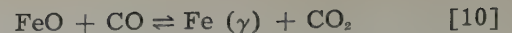
These boundaries were located as follows:

NJ-4: Line recommended by Darken and Gurry<sup>3</sup> from melting point of wüstite to point 4 at the fayalite eutectic temperature which was found by Bowen and Schairer.<sup>2</sup>

4-5: Curve from point 4 on line NJ-4 to point 5 recommended by Darken,<sup>5</sup> based on data by Schenck, Franz, and Laymann,<sup>12</sup> Bowen and Schairer,<sup>2</sup> and Darken and Gurry. Points a, b, c, and d located by extrapolation of present experimental data to fayalite-saturation temperatures which were read from Bowen and Schairer's constitution diagram.

5-D: Straight line from point 5 through experimental points of present investigation.

C-NJ: Straight line recommended by Darken and Gurry,<sup>4</sup> to point C at the melting point of oxygen-saturated iron as determined by Chipman and Marshall.



Letting  $k$  represent the equilibrium constant:

$$a_{\text{FeO}} = \frac{1}{k} \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \quad [11]$$

for the slags in equilibrium with  $\gamma$ -Fe ( $a_{\text{Fe}} = 1$ ). Choice of an appropriate standard state for FeO is a little troublesome. In the first place, a pure FeO phase does not exist. Second, in the whole range of iron-saturated melts studied there is no solution whose composition does not change with temperature. That is, the experimental data are for compositions and temperatures on the iron-saturation surface in the ternary constitution diagram, and this surface is not a vertical section. However, the composition variation with temperature is small enough so that no serious difficulties are introduced by taking the standard state of FeO as the  $\gamma$ -Fe-saturated, 0 pct SiO<sub>2</sub> slag; that is, the pure Fe-O melt in equilibrium with  $\gamma$ -Fe. Adopting this standard state, the equilibrium constant  $k$  for reaction 10 can be evaluated from Darken and Gurry's recommended equilibrium values of  $p_{\text{CO}_2}/p_{\text{CO}}$  for the system of liquid iron oxide and  $\delta$ -Fe, see Table VIII, ref. 4, applying the small correction for the change from  $\delta$ -Fe to  $\gamma$ -Fe. These calculations give:

$$\log_{10} k = \frac{2640}{T} - 2.157 \quad [12]$$

Combining this relation with eq 11 gives:

$$\log a_{\text{FeO}} = \log \frac{p_{\text{CO}_2}}{p_{\text{CO}}} - \frac{2640}{T} + 2.157 \quad [13]$$

This equation can now be used to calculate  $a_{\text{FeO}}$  for all the experimentally determined equilibria. Results of these calculations for the 33 equilibrium runs are given in Table V. Table V also includes calculated mol fractions taking Fe, O, and SiO<sub>2</sub> as the three slag components ( $N_{\text{Fe}} + N_{\text{O}} + N_{\text{SiO}_2} = 1$ ).

The outstanding and in fact entirely unexpected feature of the set of values of  $a_{\text{FeO}}$  for slags of different SiO<sub>2</sub> contents is that for a given pct SiO<sub>2</sub>,  $a_{\text{FeO}}$  does not vary with temperature. For five out of the seven slags for which  $a_{\text{FeO}}$  was measured at different temperatures,  $a_{\text{FeO}}$  is constant to within about 1 pct as the temperature varies. For the 17.2 pct SiO<sub>2</sub> slag,  $a_{\text{FeO}}$  increases only about 2 pct from 1264° to 1364°C. The largest variation, for the 27.1 pct SiO<sub>2</sub> slag, is an increase of about 5 pct in  $a_{\text{FeO}}$  over a range of 100°, and in the absence of a definite trend for the other slag compositions it appears that this variation might be a result of experimental error. From eq 13 used in calculating  $a_{\text{FeO}}$  from the data, constant  $a_{\text{FeO}}$  means that a plot of  $\log p_{\text{CO}_2}/p_{\text{CO}}$  against  $10^4/T$  will have a slope of 0.2640. Accordingly, the representation of the data in Fig. 3 and Fig. 7 by straight lines of slope 0.2640, to which attention was called previously, reflects the conclusion that for a given slag  $a_{\text{FeO}}$  does not vary with temperature, within experimental error.

The relation of  $a_{\text{FeO}}$  to temperature for slags saturated with  $\gamma$ -iron and wüstite can be expressed by combining eqs 8 and 13 to obtain:

$$\log a_{\text{FeO}} = -\frac{1790}{T} + 1.089 \quad [14]$$

As can be seen in Table Vb, the experimental figures for  $a_{\text{FeO}}$  fit this equation based on Darken and Gurry's work to within about 2 pct.

D-C: Straight line from point C, with slope corrected slightly from the vertical to allow for effect of oxygen on the melting point of iron. Point D found by intersection of lines from C and from 5. This location of D at 1530°C,  $\log p_{\text{CO}_2}/p_{\text{CO}} = -1.118$  ( $p_{\text{CO}_2}/p_{\text{CO}} = 0.076$ ) is to be compared with the estimate given by Darken<sup>5</sup> of 1525°C,  $\log p_{\text{CO}_2}/p_{\text{CO}} = -1.16$  ( $p_{\text{CO}_2}/p_{\text{CO}} = 0.069$ ).

Attention should be called to the fact that the lines drawn for the slags of varying SiO<sub>2</sub> content all have slopes of 0.264 and thus are substantially parallel to line NJ-C which has a slope of 0.260. The slight difference in slope of 0.004 is an arbitrary difference as far as the experimental data are concerned, but is the difference calculated on the assumption that the slope was affected only by the change from  $\gamma$  to  $\delta$  iron at 1400°C.

### Thermodynamic Calculations

**FeO Activity:** Calculation of  $a_{\text{FeO}}$  from the experimental data requires the choice of a standard state of unit activity for FeO and data on the equilibrium constant for the reaction:

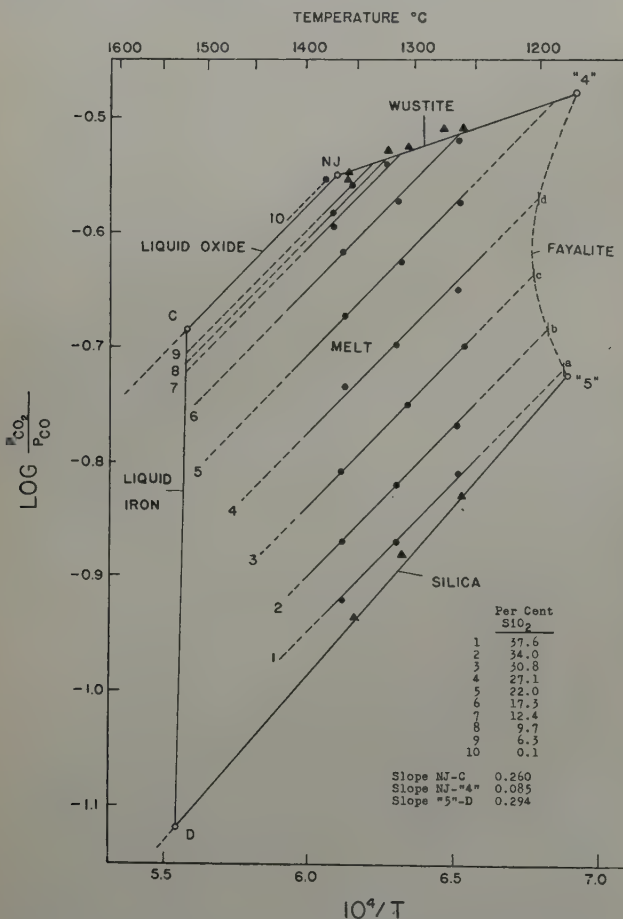


Fig. 7—Log  $p_{\text{CO}_2}/p_{\text{CO}}$  vs.  $10^4/T$  showing the field of stability of Fe-Si-O melts in equilibrium with solid Fe. Coordinates of the invariant points are tabulated below:

| Invariant Point* | Log $\frac{p_{\text{CO}_2}}{p_{\text{CO}}}$ | $\frac{\text{CO}_2}{\text{CO}}$ | $\frac{10^4}{T}$ | Temperature, °C |
|------------------|---------------------------------------------|---------------------------------|------------------|-----------------|
| NJ               | -0.550                                      | 0.282                           | 6.08             | 1371            |
| 4                | -0.480                                      | 0.331                           | 6.91             | 1175            |
| 5                | -0.724                                      | 0.189                           | 6.88             | 1180            |
| D                | -1.118                                      | 0.076                           | 5.55             | 1530            |
| C                | -0.685                                      | 0.206                           | 5.57             | 1524            |

\* Labeling of points follows Darken and Gurry<sup>4</sup> and Darken.<sup>5</sup>



Similarly, the relation of  $a_{\text{FeO}}$  to temperature for slags saturated with  $\gamma$ -iron and  $\text{SiO}_2$  is found, combining eq 9 and 13:

$$\log a_{\text{FeO}} = \frac{300}{T} - 0.590 \quad [15]$$

In Table Vc, the values of  $a_{\text{FeO}}$  calculated by this equation are given for comparison with the experimental values. Extrapolating the data to the melting point of iron by means of the equation gives  $a_{\text{FeO}} = 0.377$  for silica-saturated iron-silicate slags at  $1530^\circ\text{C}$ . This figure is in good agreement with the value of 0.39 found at  $1600^\circ\text{C}$  by Chipman and Gokcen,<sup>13</sup> and both the newer figures are a little higher than an estimate of about 0.33 based on Körber and Olson's work.<sup>14</sup>

Fig. 8 shows graphically the variation of  $a_{\text{FeO}}$  with weight pct  $\text{SiO}_2$ . One curve adequately represents the results for all the temperatures investigated since, as already discussed, no variation of  $a_{\text{FeO}}$  with temperature was established within experimental error. For comparison, a dotted curve is given, showing how  $a_{\text{FeO}}$  would vary with pct  $\text{SiO}_2$  if the slags were ideal binary solutions of FeO and  $\text{SiO}_2$ . It should be noted that the curves also represent

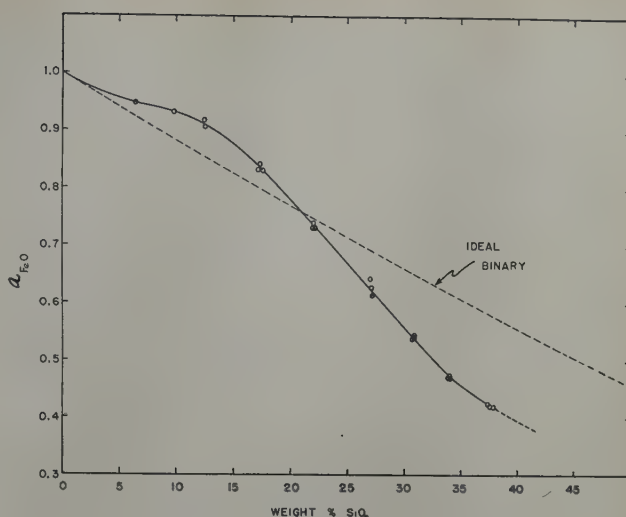


Fig. 8—Variation of  $a_{\text{FeO}}$  with percent  $\text{SiO}_2$ .

oxygen activity, if  $a_o = 1$  for the 0 pct  $\text{SiO}_2$  melt, because  $a_{\text{Fe}}$  is constant for the system and  $a_{\text{FeO}} \propto a_{\text{Fe}} \times a_o$ .

**FeO- $\text{SiO}_2$  Constitution Diagram:** The FeO-activity data in Table V and Fig. 8 can be used to locate the liquidus curves for wüstite and silica in the FeO- $\text{SiO}_2$  constitution diagram. For each of the seven temperatures of wüstite-saturation measurements in Table Vb, the corresponding pct  $\text{SiO}_2$  in the melt is found from the activity curve in Fig. 8 as the abscissa corresponding to the measured value of  $a_{\text{FeO}}$  for wüstite saturation at this temperature. Similarly, the values of pct  $\text{SiO}_2$  in the melt for  $\text{SiO}_2$  saturation are found from Fig. 8 and Table Vc. The  $\text{SiO}_2$  percentages read from Fig. 8 in this way are given in parentheses in Tables Vb and Vc.

In Fig. 9 the results of the present investigation are compared with those of Bowen and Schairer. It should be kept in mind that this diagram is not a true binary diagram. Also, Fig. 9 differs from the familiar published diagram of Bowen and Schairer in that the abscissa is actual weight pct  $\text{SiO}_2$  as determined by analysis. It can be seen that the results of the present investigation agree well with the previous results of Bowen and Schairer.

**$\text{SiO}_2$  Activity:** Activities of  $\text{SiO}_2$  can be calculated by a Gibbs-Duhem integration. Taking the components of the slags as Fe, O, and  $\text{SiO}_2$ :

$$N_o d \log a_o + N_{\text{SiO}_2} d \log a_{\text{SiO}_2} + N_{\text{Fe}} d \log a_{\text{Fe}} = 0 \quad [16]$$

The third term drops out for the slags studied in this work because  $a_{\text{Fe}}$  is constant. Also, because  $a_{\text{Fe}}$  is constant,  $d \log a_o = d \log a_{\text{FeO}}$ . Hence, the Gibbs-Duhem equation becomes:

$$N_o d \log a_{\text{FeO}} + N_{\text{SiO}_2} d \log a_{\text{SiO}_2} = 0 \quad [17]$$

Integrating:

$$\log a_{\text{SiO}_2} = - \int \frac{N_o}{N_{\text{SiO}_2}} d \log a_{\text{FeO}} \quad [18]$$

Taking solid silica (tridymite) as the standard state for which  $a_{\text{SiO}_2} = 1$ , this integration has been carried out for the whole range of slag compositions at an arbitrarily chosen temperature of  $1350^\circ\text{C}$ . Data for the integration are tabulated in Table VI, and the activities of FeO and  $\text{SiO}_2$  are plotted against  $N_{\text{SiO}_2}$  in Fig. 10. The dashed curves indicate the behavior to be expected if the slags were binary solutions of FeO (so that  $n_o = n_{\text{Fe}} = n_{\text{FeO}}$ ) and  $\text{SiO}_2$  and

Table V. Activities of FeO

| Run No.                                                      | Temperature, °C | $\text{SiO}_2$ , Pct | $N_{\text{SiO}_2}$ | $N_{\text{Fe}}$ | $N_o$ | $\log a_{\text{FeO}}$ | $a_{\text{FeO}}$ |
|--------------------------------------------------------------|-----------------|----------------------|--------------------|-----------------|-------|-----------------------|------------------|
| <b>a. Slags of Varying <math>\text{SiO}_2</math> Content</b> |                 |                      |                    |                 |       |                       |                  |
| 1                                                            | 1263            | 37.4                 | 0.263              | 0.367           | 0.370 | -0.372                | 0.425            |
| 2                                                            | 1315            | 37.6                 | 0.265              | 0.367           | 0.368 | -0.374                | 0.422            |
| 3                                                            | 1364            | 37.9                 | 0.267              | 0.366           | 0.367 | -0.376                | 0.421            |
| 4                                                            | 1264            | 34.1                 | 0.236              | 0.380           | 0.384 | -0.328                | 0.470            |
| 5                                                            | 1315            | 34.0                 | 0.235              | 0.381           | 0.384 | -0.324                | 0.474            |
| 6                                                            | 1364            | 33.85                | 0.235              | 0.382           | 0.383 | -0.325                | 0.473            |
| 7                                                            | 1258            | 30.7                 | 0.209              | 0.393           | 0.398 | -0.266                | 0.541            |
| 8                                                            | 1305            | 30.8                 | 0.210              | 0.394           | 0.396 | -0.266                | 0.541            |
| 9                                                            | 1365            | 30.9                 | 0.211              | 0.393           | 0.396 | -0.264                | 0.545            |
| 10                                                           | 1264            | 27.2                 | 0.182              | 0.405           | 0.413 | -0.211                | 0.615            |
| 11                                                           | 1315            | 27.1                 | 0.182              | 0.406           | 0.412 | -0.203                | 0.627            |
| 12                                                           | 1362            | 27.05                | 0.181              | 0.406           | 0.413 | -0.192                | 0.644            |
| 13                                                           | 1262            | 22.2                 | 0.145              | 0.423           | 0.432 | -0.136                | 0.731            |
| 14                                                           | 1312            | 21.9                 | 0.143              | 0.425           | 0.432 | -0.135                | 0.732            |
| 15                                                           | 1362            | 21.95                | 0.143              | 0.425           | 0.432 | -0.131                | 0.740            |
| 16                                                           | 1264            | 17.5                 | 0.112              | 0.437           | 0.451 | -0.081                | 0.831            |
| 17                                                           | 1314            | 17.15                | 0.110              | 0.440           | 0.450 | -0.079                | 0.834            |
| 18                                                           | 1364            | 17.3                 | 0.111              | 0.439           | 0.450 | -0.073                | 0.845            |
| 19                                                           | 1324            | 12.5                 | 0.078              | 0.453           | 0.469 | -0.037                | 0.919            |
| 20                                                           | 1374            | 12.45                | 0.078              | 0.456           | 0.466 | -0.042                | 0.907            |
| 21                                                           | 1374            | 9.75                 | 0.060              | 0.461           | 0.479 | -0.030                | 0.933            |
| 22                                                           | 1356            | 6.3                  | 0.038              | 0.471           | 0.491 | -0.023                | 0.948            |
| 23                                                           | 1407            | 0.1                  | 0.001              | 0.491           | 0.508 | +0.007                | 1.015            |
| <b>b. Wüstite-saturated Slags</b>                            |                 |                      |                    |                 |       |                       |                  |
| 24                                                           | 1259            | (17.2)               |                    |                 |       | -0.076                | 0.839 (0.833)*   |
| 27                                                           | 1275            | (15.1)               |                    |                 |       | -0.058                | 0.875 (0.857)*   |
| 25                                                           | 1302            | (13.1)               |                    |                 |       | -0.044                | 0.904 (0.895)*   |
| 28                                                           | 1306            | (12.3)               |                    |                 |       | -0.040                | 0.912 (0.902)*   |
| 26                                                           | 1323            | (7.5)                |                    |                 |       | -0.025                | 0.944 (0.929)*   |
| 29                                                           | 1357            | (3.9)                |                    |                 |       | -0.010                | 0.977 (0.980)*   |
| 30                                                           | 1358            | (2.1)                |                    |                 |       | -0.017                | 0.962 (0.982)*   |
| <b>c. Silica-saturated Slags</b>                             |                 |                      |                    |                 |       |                       |                  |
| 31                                                           | 1260            | (39.3)               |                    |                 |       | -0.394                | 0.403 (0.404)**  |
| 32                                                           | 1310            | (39.0)               |                    |                 |       | -0.391                | 0.406 (0.397)**  |
| 33                                                           | 1352            | (40.2)               |                    |                 |       | -0.402                | 0.396 (0.394)**  |
|                                                              | 1180†           | (38.5)               |                    |                 |       | -0.383                | 0.414 (0.413)**  |

\* Values in parentheses calculated from:

$$\log a_{\text{FeO}} = - \frac{1790}{T} + 1.089$$

\*\* Values in parentheses calculated from:

$$\log a_{\text{FeO}} = \frac{300}{T} - 0.590$$

† Based on previous work; see Table IV.

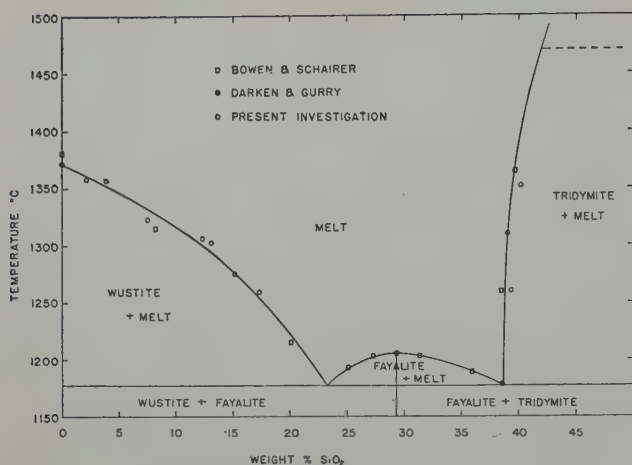


Fig. 9—Constitution diagram showing liquidus data for iron-silicate slags in equilibrium with solid Fe.

if the activities were directly proportional to mol fractions. The hypothetical curve for  $a_{FeO}$  is based on the assumption that  $a_{FeO}$  equals mol fraction of FeO in the binary, while the hypothetical curve for  $a_{SiO_2}$  is based on the assumptions that  $a_{SiO_2} = 1$  for silica saturation and that  $a_{SiO_2}$  is proportional to mol fraction  $SiO_2$  calculated on the binary basis. The relative positions of the actual activity curves and the hypothetical binary curves show that the behavior of the system does not even approximate that of an ideal binary solution of FeO and  $SiO_2$ .

**Heats of Solution:** The partial molal heat content of a substance in solution, relative to the standard state of that substance, is readily calculated from data giving the variation of the activity of that substance with temperature for the solution of given constant composition. For a ternary system, the relative partial molal heat content of one component,  $\bar{L}_1$ , is given by:

$$\bar{L}_1 = R \left( \frac{\partial \ln f_1}{\partial \left( \frac{1}{T} \right)} \right)_{N_1, \frac{N_2}{N_3}} - R \left( \frac{\partial \ln f_1^\circ}{\partial \left( \frac{1}{T} \right)} \right)_{N_1, \frac{N_2}{N_3}} \quad [19]$$

in which  $R$  is the gas constant,  $T$  is the absolute temperature, and  $f_1$  and  $f_1^\circ$  represent the fugacities of the substance in the solution and in the standard state, respectively. Since  $a_1 = f_1/f_1^\circ$ , eq 19 ordinarily reduces to:

$$\bar{L}_1 = R \left( \frac{\partial \ln a_1}{\partial \left( \frac{1}{T} \right)} \right)_{N_1, \frac{N_2}{N_3}} \quad [20]$$

However, the activity-temperature data of the present investigation cannot be used directly with eq 20 because both the standard state of FeO and all the slags studied were solutions whose compositions varied with temperature to meet the condition of saturation with solid iron. The following approximation can be used to estimate the partial molal heat content of FeO in the slag relative to that in the pure Fe-O melt in equilibrium with solid iron.

$$\bar{L}_{FeO} = R \left( \frac{\partial \ln a_{FeO}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, \frac{N_O}{N_{Fe}}} = \text{approximately} \quad R \left( \frac{\partial \ln a_{FeO}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, a_{FeO} = 1} \quad [21]$$

Since experimentally it was found that  $a_{FeO}$  does not

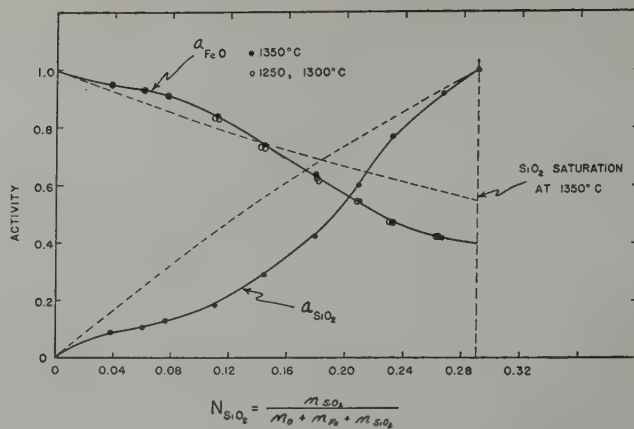


Fig. 10— $a_{FeO}$  and  $a_{SiO_2}$  vs.  $N_{SiO_2}$  for Fe-saturated iron-silicate slags.

vary with temperature for given  $N_{SiO_2}$  in Fe-saturated slags, eq 21 leads to the result:

$$\bar{L}_{FeO} = 0$$

over the whole range of slag compositions. The probable error in  $\bar{L}_{FeO}$  from the experimental data is estimated to be  $\pm 400$  cal.

By applying the methods of partial differential calculus the error in eq 21 can be related to: 1—The rate of change of  $a_{FeO}$  with  $N_O/N_{Fe}$  at constant temperature, and 2—the rate of change of  $N_O/N_{Fe}$  with temperature for Fe saturation. Estimates of these two rates based mainly on Darken and Gurry's data indicate that the error in the approximate eq 21 probably is under 1000 cal per mol. This error is thus of the same order of magnitude as the experimental error.

Estimates of heats of solution of  $O_2$  and Fe cannot be made satisfactorily from the experimental data on Fe-saturated slags, and must await further data on the effect of  $N_O/N_{Fe}$  on  $a_{Fe}$  and  $p_{O_2}$ .

The partial molal heat content of  $SiO_2$  relative to the solid can be estimated by an approximation similar to that used in estimating  $\bar{L}_{FeO}$ :

$$\bar{L}_{SiO_2} = R \left( \frac{\partial \ln a_{SiO_2}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, \frac{N_O}{N_{Fe}}} = \text{approximately} \quad R \left( \frac{\partial \ln a_{SiO_2}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, a_{Fe} = 1} \quad [22]$$

Applying the principles of partial differentiation, the right-hand number of eq 22 can be written:

$$R \left( \frac{\partial \ln a_{SiO_2}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, a_{Fe}} = R \left( \frac{\partial \ln a_{SiO_2}}{\partial \ln a_{FeO}} \right)_{T, a_{Fe}} \left[ \left( \frac{\partial \ln a_{FeO}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, a_{Fe}} - \left( \frac{\partial \ln a_{FeO}}{\partial \left( \frac{1}{T} \right)} \right)_{a_{SiO_2}, a_{Fe}} \right] \quad [23]$$

The Gibbs-Duhem relation for the system, eq 17 gives:

$$\left( \frac{\partial \ln a_{SiO_2}}{\partial \ln a_{FeO}} \right)_{T, a_{Fe} = 1} = - \frac{N_O}{N_{SiO_2}} \quad [24]$$

Experimentally it was found that:

$$\left( \frac{\partial \ln a_{FeO}}{\partial \left( \frac{1}{T} \right)} \right)_{N_{SiO_2}, a_{Fe} = 1} = 0 \quad [25]$$



Table VI. Data\* of Duhem Integration for Obtaining  $\text{SiO}_2$  Activities at  $1350^\circ\text{C}$

| $\text{SiO}_2, \text{Pct}$ | $N_{\text{SiO}_2}$ | $N_{\text{O}}:N_{\text{SiO}_2}$ | $\log a_{\text{FeO}}$ | $\log a_{\text{SiO}_2}$ | $a_{\text{SiO}_2}$ |
|----------------------------|--------------------|---------------------------------|-----------------------|-------------------------|--------------------|
| Sat'd                      |                    |                                 | -0.402                | 0                       | 1.000              |
| 37.9                       | 0.267              | 1.375                           | -0.376                | -0.036                  | 0.921              |
| 33.85                      | 0.235              | 1.63                            | -0.325                | -0.112                  | 0.773              |
| 30.9                       | 0.211              | 1.88                            | -0.264                | -0.219                  | 0.604              |
| 27.05                      | 0.181              | 2.28                            | -0.192                | -0.369                  | 0.428              |
| 21.95                      | 0.143              | 3.02                            | -0.131                | -0.531                  | 0.294              |
| 17.3                       | 0.111              | 4.05                            | -0.073                | -0.734                  | 0.185              |
| 12.45                      | 0.078              | 5.98                            | -0.042                | -0.884                  | 0.131              |
| 9.75                       | 0.060              | 8.00                            | -0.030                | -0.968                  | 0.108              |
| 6.3                        | 0.038              | 12.9                            | -0.023                | -1.041                  | 0.091              |
| 0                          | 0                  | $\infty$                        | 0.000                 | $-\infty$               | 0.000              |

\* Figures in first four columns are based on data taken from Table V for temperatures ranging from  $1352^\circ$  to  $1373^\circ\text{C}$ . Values of  $\log a_{\text{SiO}_2}$  in the fifth column were obtained by graphical integration, using a large plot of  $\log a_{\text{FeO}}$  vs.  $N_{\text{O}}:N_{\text{SiO}_2}$ .

The experimental data for  $\text{SiO}_2$ -saturated slags, as represented by eq 15, give:

$$\left( \frac{\partial \log_{10} a_{\text{FeO}}}{\partial \left( \frac{1}{T} \right)} \right)_{a_{\text{SiO}_2}=1, a_{\text{Fe}}=1} = 300 \quad [26]$$

Substituting eqs 24, 25, and 26 into eq 23, and using an average value of  $N_{\text{O}}/N_{\text{SiO}_2} = 1.3$  for  $\text{SiO}_2$ -saturated slags, the partial molal heat content of the  $\text{SiO}_2$  in  $\text{SiO}_2$ -saturated slags relative to the heat content of solid  $\text{SiO}_2$  is found:

$$\bar{L}_{\text{SiO}_2 (\text{solid})} = \text{approximately} + 1700 \text{ cal}$$

This figure is about the same as the heat of fusion of silica, so that within the combined experimental and estimation error, the partial molal heat of solution of liquid  $\text{SiO}_2$  in silica and iron-saturated slag appears to be nil. Since both  $\bar{L}_{\text{SiO}_2 (\text{liq.})}$  and  $\bar{L}_{\text{FeO} (\text{liq.})}$  are estimated to be nil, it follows that the heat of formation of the liquid slag from liquid  $\text{SiO}_2$  and liquid  $\text{FeO}$ , that is, the heat of mixing, is nil.

**Constitution of Iron-Silicate Slags:** Several attempts have been made to interpret the thermodynamic data in terms of constitution models of the slag. By far the best fit has been obtained by an ionic theory of slag constitution, similar in broad lines to that proposed by Chipman and Chang<sup>15</sup> to interpret the behavior of liquid iron oxides. However, this theory requires further development and can well await the availability of additional data from work now in progress on a wider range of slag compositions in the ternary system  $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$ .

### Summary

The oxygen activities of liquid iron-silicate slags in equilibrium with  $\gamma$ -iron, ranging in composition from 0 pct to about 40 pct  $\text{SiO}_2$  (silica-saturation), have been determined at temperatures from  $1250^\circ$  to  $1400^\circ\text{C}$ . The experimental method consisted in bubbling  $\text{CO}_2\text{-CO}$  mixtures through the slags contained in iron crucibles. Compositions of incoming and outgoing gases were compared as a test of equilibrium, and the composition of the incoming gas was adjusted until equilibrium was attained. Equilibrium determinations were also made for the system slag: $\gamma$ -iron:wüstite:gas and for the system slag: $\gamma$ -iron:silica:gas.

The experimental results have been carefully correlated with the previous work of Bowen and Schairer on the same system, with the results of Darken and Gurry on the iron-oxygen system, and

with the work of Darken on the  $\text{Fe-Si-O}$  system. The results of the present investigation were found to be consistent with the previous work and thus indirectly afford some confirmation of the findings of the earlier investigation cited. These correlations are summarized in Figs. 7 and 9, which describe the system of iron-saturated, iron silicate slags in terms of the oxygen-activity temperature relationships and the constitution diagram, respectively.

From the experimental data, activities of  $\text{FeO}$  and  $\text{SiO}_2$  were calculated. It was found that the activity-composition relationships deviate considerably from those to be expected for an ideal binary solution of  $\text{FeO}$  and  $\text{SiO}_2$ . However, the partial molal heat of solution of  $\text{FeO}$  from the liquid iron-oxide melt in equilibrium with solid iron into the slags was estimated from the activity-temperature data to be zero. Also, the partial molal heat of solution of liquid silica (metastable) in silica-saturated slags was estimated to be zero.

### Acknowledgment

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## Some Notes on the Barley Shell Structure in Iron-Silicon Alloys

by R. V. Riley

IN the metallographic examination of the alloys of iron and silicon, several investigators<sup>1-7</sup> have reported on the occurrence of an unusual type of etched structure, particularly in the alloys of higher silicon content. This, the so-called "barley shell" structure, has been observed with iron-silicon alloys over a wide range of silicon content, and under certain circumstances it can be seen upon the micro-sections of pure iron.

The barley shell structure may be demonstrated most easily with iron-silicon alloys in the range 8 to 20 pct Si after etching in a hydrofluoric acid base etchant. Two etchants which produce the structure are: Corson's reagent, which is 2 parts hydrofluoric acid, 1 part nitric acid, and 2 parts glycerol; and picric acid reagent, which is 1 part hydrofluoric acid and 1 part saturated solution of picric acid in alcohol. Both when freshly prepared and used for etching commercial silicon-iron alloys containing 14 to 16 pct Si, invariably produce the barley shell structure shown in Fig. 1a. It is now well known that the barley shell structure is a pseudomorph and the true structure of an alloy of this composition consists of a single phase of silico-ferrite together with graphite as shown in Fig. 1b.

Lower silicon alloys and even pure electrolytic iron may also be etched in the above reagents to give the barley shell provided the etchant has been either: 1—Stored in contact with glass or silica, or 2—used previously for etching an iron containing silicon.

Pure iron etched in perfectly pure hydrofluoric acid base etchants free from silicon contamination gives a normal structure free from the barley shells. Therefore, although the hydrofluoric acid in the reagent primarily is responsible for the barley shells, silicon, or its compounds, also must be present, either in the etching reagent or in the specimen.

It was of considerable interest to the author to read the paper by Wachtell,<sup>7</sup> in which the barley shell etch was deliberately used for the identification of the boundaries of high and low silicon areas in diffusion experiments made upon laminate bars or compacted and sintered pure iron and ferrosilicon powders. This method of utilizing the barley shell etch is novel and in the hands of the investigator gave a useful differentiation between the high and low silicon areas in those specimens. For the reasons already given, however, the technique is not to be regarded as of universal application. Misleading results might be obtained, for example, if two or more specimens were etched in the same etchant. Fresh pure reagents only must be used each time. Provided this is done and the investigators are well aware of the limitations of the

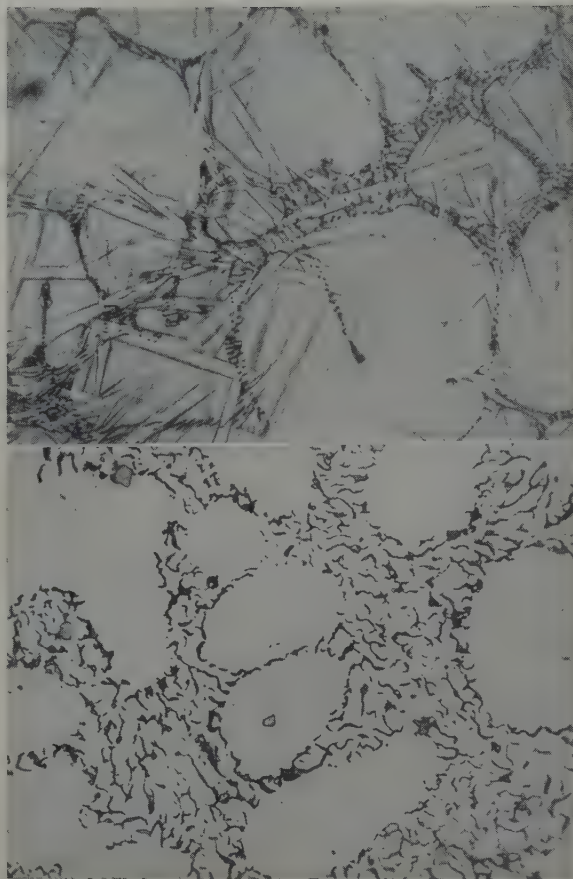


Fig. 1a (upper)—Barley shell structure in commercial 15 pct Si-Fe alloy.

Fig. 1b (lower)—True structure of silico-ferrite and graphite in commercial 15 pct Si-Fe alloy.

X600. Area reduced approximately 50 pct for reproduction.

method, then the barley shell pseudomorph can be made of limited use in distinguishing between higher and lower silicon areas in a microspecimen of a ferrous material. The greatest of care must be exercised in the interpretation of the results which may be regarded as qualitative only and may, in fact, not be specific to silicon alloys.

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# Metallurgy of Cobalt Production

## From Cupriferous Pyrite

by Sanai Nakabe

Japanese wartime economy demanded domestic cobalt production. This paper describes a process operated for two years at the Besshi mine and smelter on extremely low grade (0.1 pct Co) pyrite concentrates obtained from copper ore. The steps in the process were roasting, leaching, precipitation, reduction fusion to crude cobalt, and finally refining by electrolysis to 99+ pct.

COBALT ore deposits in Japan are all small and of poor grade. In the past, a small amount of cobalt has been produced from the best portions of a few of these deposits, and very little production is expected in the future. In addition to these lean cobalt ores, cobalt is present in the cupriferous pyrite which is fairly abundant although of low grade, as is shown in Table I. Considerable cobalt is expected from these deposits because of their extent.

Cobalt cannot be exclusively recovered economically from ore of this type; however, if means could be devised to recover it as a byproduct of copper production, a fairly large production at reasonable cost could be expected from Japanese sources. It was along this line that the research work was done.

### Selection of Suitable Process

The process for extracting cobalt differs from ore to ore according to their composition. The difficulty in cobalt metallurgy arises from the fact that chemically cobalt resembles many such common metals as Mn, Fe, Ni, Cu, and Zn, associated with it in the ores. In the present case the most serious difficulties were:

- 1—Extremely low grade ore, 0.1 pct Co.
- 2—The large proportion of iron accompanying

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Table I. Some Examples of Cobalt Content of Japanese Cupriferous Pyrite

| Mine      | Co, Pct | Cu, Pct | Fe, Pct | S, Pct |
|-----------|---------|---------|---------|--------|
| Ismori    | 0.11    | 1.74    | 39.52   | 44.25  |
| Shirataki | 0.05    | 1.60    | 44.51   | 50.77  |
| Kotsu     | 0.22    | 2.80    | 42.51   | 49.09  |
| Chihara   | 0.04    | 19.89   | 29.75   | 33.75  |
| Kune      | 0.19    | 8.64    | 40.29   | 45.36  |
| Motoyasu  | 0.10    | 2.47    | 44.18   | 50.34  |
| Yanahara  | Trace   | 0.55    | 45.51   | 51.47  |
| Makimine  | 0.17    | 5.40    | 42.57   | 46.10  |
| Sazare    | 0.04    | 5.49    | 39.96   | 45.69  |
| Besshi    | 0.10    | 4.72    | 40.84   | 45.55  |

cobalt and its close similarity in chemical behavior.

3—The fairly large proportion of zinc and manganese and their chemical similarity to cobalt.

The recovery of cobalt oxide as a byproduct of the hydrometallurgy of copper had been attempted in Japan but was stopped after a short period because it proved uneconomical. The literature disclosed no method for the recovery of cobalt from cobaltiferous copper pyrite and it was therefore necessary to devise a new process.

The following basic principles were considered in selecting the process:

1—A major alteration in copper production methods should not be necessary.

2—The first step should be the extraction of cobalt leaving the large quantity of iron unaffected. For this purpose wet metallurgy would be preferred.

Table II. Distribution of Cobalt to Intermediates in Copper Smelting

|                     | Cu,<br>Pct | Fe,<br>Pct | Co,<br>Pct | S,<br>Pct | Co<br>Quantity |
|---------------------|------------|------------|------------|-----------|----------------|
| Crude ore           | 1.17       | 19.16      | 0.03       | 9.98      | 100            |
| Copper concentrate  | 10.36      | 34.51      | 0.10       | 36.47     | 37             |
| Pyrite concentrate  | 0.32       | 41.52      | 0.10       | 45.05     | 30             |
| Flotation tailing   | 0.09       | 13.05      | 0.01       | 2.36      | 26             |
| Blast furnace matte | 35         | 40         | 0.3        | 23        | 20             |
| Blast furnace slag  | 0.3        | 35         | 0.06       |           | 35             |
| Converter slag      | 2          | 55         | 0.4        |           | 20             |
| Blister copper      | 98         |            | 0.002      |           | 0.1            |

3—A crude precipitate of cobalt would be satisfactory in order to avoid a large expenditure in chemically treating a huge volume of leach solution to obtain a pure precipitate.

4—The crude cobalt precipitate would be further refined. It would not matter if the process became somewhat complicated at this point because the quantity of material for treatment would be decreased markedly.

### Selection of Direct Raw Material

As the raw material it was first necessary to select an intermediate product from the copper extraction process. Four were selected, namely, pyrite concentrate from the flotation, matte from the blast furnace, slag from the same, and slag from the converter.

Three different processes were devised for treating concentrate, matte, and slag. The first one for treating the concentrate proved to be best suited for the circumstances at Besshi mine and the Japanese wartime economy. This process was operated on a plant scale and will be reported here, but the other two were not developed to plant size although they proved to be valuable in those cases where somewhat more cobalt is contained in the raw material in copper smelting. The compositions of several intermediate products at the Besshi smelter are shown in Table II. In order to make it pay it is desirable that a process for treating a poor raw material should have some extra merits in addition to the principal one which, in this case, aims at cobalt recovery. By treating iron concentrate, a quantity of copper would be recovered and, at the same time, the quality of the leached residue, by the elimination of copper, would be enhanced.

### Flotation

Usually no distinct cobalt mineral is identified in the ores and it is supposed that cobalt exists in solid solution in the pyrite crystal, displacing some of the iron atoms. Whether there is any difference in cobalt content between chalcopyrite and iron pyrite is open to question. In the case of the Besshi ore there is little difference according to the analyses of the two kinds of concentrate produced at the flotation mill, Table III. It was concluded therefore that no change in the process of flotation was necessary and both

Table III. Distribution of Cobalt by Flotation

|                    | Co,<br>Pct | Cu,<br>Pct | Fe,<br>Pct | S,<br>Pct | Production<br>Ratio, Calcu-<br>lated | CuFeS <sub>2</sub> , FeS <sub>2</sub> ,<br>Calculated |
|--------------------|------------|------------|------------|-----------|--------------------------------------|-------------------------------------------------------|
| Feed ore           | 0.03       | 1.17       | 19.16      | 9.98      | 100                                  | 3.4                                                   |
| Copper concentrate | 0.10       | 10.36      | 34.51      | 36.47     | 11                                   | 29.9                                                  |
| Pyrite concentrate | 0.10       | 0.32       | 41.52      | 45.07     | 9                                    | 0.9                                                   |
| Tailing            | 0.01       | 0.09       | 13.05      | 2.36      | 80                                   | 0.5                                                   |

Table IV. Successive Change in Roasting

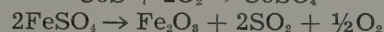
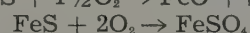
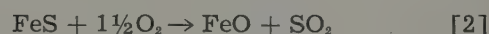
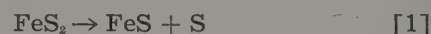
| Hearth<br>No. | Residual<br>S,<br>Pct | Water-Soluble Ingredients |            |            |           |
|---------------|-----------------------|---------------------------|------------|------------|-----------|
|               |                       | Co,<br>Pct                | Cu,<br>Pct | Fe,<br>Pct | S,<br>Pct |
| 3             | 27.45                 | 0.010                     | 0.040      | 0.143      | 0.77      |
| 4             | 20.62                 | 0.012                     | 0.058      | 0.402      | 0.96      |
| 5             | 5.18                  | 0.040                     | 0.168      | 0.347      | 1.24      |
| 6             | 3.07                  | 0.053                     | 0.245      | 0.782      | 2.45      |
| 7             | 1.90                  | 0.068                     | 0.291      | 0.468      | 1.56      |
| 8             | 1.81                  | 0.067                     | 0.283      | 0.226      | 1.36      |

concentrates must be treated separately for cobalt production.

### Roasting

Various methods were examined to render cobalt in pyrite soluble in water or dilute acid, and it was finally decided that an oxidizing roast was the best practical method if sufficient attention was paid to operation. Roasting for sulphuric acid production needs no special regulation, but for cobalt extraction careful control in roasting is necessary. The most important factor in roasting regulation is the temperature control which will be explained.

Practically all of the soluble cobalt in the cinder proved to be cobalt sulphate and not oxide. This was true with acid leaching as well as with water leaching not only for oxidizing roasts but for all the roasting methods tried. Therefore, it was most desirable to convert as much into sulphate as possible. Most of the cobalt sulphate was formed near the final roasting stage according to the numerical order of the following equations. An example of the successive change is given in Table IV which shows analyses of samples taken from each hearth of a Herreshof-type roaster. The diameter of each of the eight hearths was 9 ft 6 in.



Cobalt sulphate was not formed in the rapid oxidation of pyrite resulting in a black cinder. One of

Table V. Ferrite Formation

| Heating<br>Temperature,<br>°C | Water-Soluble<br>Quantities |       | H <sub>2</sub> SO <sub>4</sub><br>Leach of<br>Residue,<br>Co, G | Final<br>Residue,<br>Co, G |
|-------------------------------|-----------------------------|-------|-----------------------------------------------------------------|----------------------------|
|                               | Co, G                       | Fe, G |                                                                 |                            |
| 500                           | 0.116                       | 0.001 | 0.001                                                           | 0.006                      |
| 550                           | 0.111                       | Trace | Trace                                                           | 0.010                      |
| 600                           | 0.059                       | Trace | Trace                                                           | 0.067                      |
| 650                           | 0.046                       | 0.001 | 0.001                                                           | 0.084                      |
| 700                           | Trace                       | Trace | Trace                                                           | 0.123                      |

Table VI. Lack of Ferrite Formation

| Heating<br>Temperature,<br>°C | Water-Soluble Quantities |       | Solubility<br>of Co,<br>Pct |
|-------------------------------|--------------------------|-------|-----------------------------|
|                               | Co, G                    | Fe, G |                             |
| 500                           | 0.122                    | 0.003 | 90                          |
| 550                           | 0.100                    | 0.003 | 74                          |
| 600                           | 0.105                    | 0.004 | 78                          |
| 650                           | 0.100                    | 0.002 | 81                          |
| 700                           | 0.095                    | 0.002 | 70                          |



the necessary conditions, therefore, was slow oxidation through control of the temperature or air supply. This resulted in a brown cinder. Another factor was the formation of ferrite. In the presence of ferric oxide, ferrite formation begins at about 600°C and increases as the temperature rises. However, in the presence of ferrous oxide and no ferric oxide, ferrite does not form even at the high temperature of 800°C. Table V shows the formation of ferrite when a finely ground mixture of 1.5 g of Fe<sub>2</sub>O<sub>3</sub> and 1.5 g of CoSO<sub>4</sub> · 7H<sub>2</sub>O was heated for 1 hr at the indicated temperatures. The results are shown of leaching 1 g of the product in water and further leaching the residue in boiling 2 pct H<sub>2</sub>SO<sub>4</sub>. Table VI indicates the absence of ferrite formation when a similar experiment was conducted using ferrous oxide instead of ferric oxide.

The optimum roasting temperature for cobalt sulphate formation was found to be about 550°C. This was determined experimentally, Table VII, using a small electrically heated rotary kiln. The rate of formation of cobalt sulphate is low and many hours are required for a satisfactory conversion. This is shown in Table VIII which summarizes the best results obtained by leaching cinder from different furnaces. Thermal decomposition of cobalt sulphate is not appreciable at temperatures below 750° to 850°C.

In practice a Herreshof-type furnace was found best suited for the purpose. The charging rate and the air supply must be so controlled as to obtain a gradual and sufficient oxidation, and at least two of the upper hearths must be maintained at 500° to 600°C. The maximum temperature of the upper hearths usually went over 800°C but this was not detrimental to cobalt sulphate formation in the absence of Fe<sub>2</sub>O<sub>3</sub>. The conversion was about 70 pct (soluble Co 0.09 pct) under good conditions, but fell below 30 pct with poor regulation. The ore particles swelled, becoming very porous, which had a favorable effect on leaching, Table IX. The moistures of cakes obtained by vacuum filtration of slurries are shown to give a rough idea of the porosity of the particles.

Leaching

The purpose of leaching is to dissolve cobalt and copper, leaving all of the iron undissolved in the residue. The only economical solvents, in view of the

Table VII. Selection of Roasting Temperature

| Temperature,<br>°C | Water Extract |         |         |
|--------------------|---------------|---------|---------|
|                    | Co, Pct       | Cu, Pct | Fe, Pct |
| 450                | 0.060         | 0.25    | 7.95    |
| 500                | 0.067         | 0.40    | 4.05    |
| 550                | 0.096         | 0.28    | 0.27    |
| 600                | 0.083         | 0.10    | 0.01    |
| 650                | 0.027         | 0.03    | 0.01    |
| 700                | 0.006         | 0.01    | Trace   |

Table VIII. The Effect of Roasting Time

| Type of<br>Furnace | Diameter<br>Dimen-<br>sion | No. of<br>Hearths | Capac-<br>ity,<br>Tons<br>per<br>Day | Water Leaching |                    |            |            |            |
|--------------------|----------------------------|-------------------|--------------------------------------|----------------|--------------------|------------|------------|------------|
|                    |                            |                   |                                      | Stay,<br>Hr    | Color of<br>Cinder | Co,<br>Pct | Cu,<br>Pct | Fe,<br>Pct |
| Herreshof          | 19 ft 6 in.                | 8                 | 14.4                                 | 12             | Brown              | 0.10       | 0.27       | 0.15       |
| Herreshof          | 15 ft 10 in.               | 6                 | 7.2                                  | 8              | Brown              | 0.07       | 0.15       | 0.26       |
| Herreshof          | 3 ft 6 in.                 | 10                | 0.6                                  | 5              | Brown              | 0.06       | 0.24       | 0.22       |
| Rotary kiln        | 294 x 31m                  |                   | 43                                   | 2.5            | Black              | Nil        | 0.03       | 0.02       |

Table IX. Swelling of Ore Particle by Roasting

|                    | Mesh        |             |             |              |              |              | Mois-<br>ture,<br>Pct |
|--------------------|-------------|-------------|-------------|--------------|--------------|--------------|-----------------------|
|                    | +10,<br>Pct | +28,<br>Pct | +48,<br>Pct | +100,<br>Pct | +200,<br>Pct | —200,<br>Pct |                       |
| Pyrite concentrate | 0.3         | 0.0         | 4.8         | 2.1          | 16.6         | 76.5         | 10                    |
| Cinder             | 1.3         | 2.2         | 4.3         | 11.9         | 32.9         | 47.5         | 32                    |

poor grade of the raw material, would be water or dilute acid. It was concluded, after thorough experimenting, that even dilute acid was not suitable because, although it gave slightly better cobalt and copper extraction, it dissolved considerably more iron than was the case with water leaching. Grinding, heat, and increased leaching time had little effect, as shown in Tables X through XIV. Sea water could also be used, Table XV.

Cinder was classified into three parts as indicated in Table XIV, and half of each ground to —100 mesh. Both halves were water-leached for comparison.

The data in Tables X to XV lead to the conclusion that the leaching is a very simple problem, but in practice it is very important to wash the residue efficiently in order to obtain simultaneously high extraction and high concentration of the leach solution. Continuous countercurrent decantation was adopted easily because of the fine particle size. High porosity of the cinder was not conducive to good washing because in a thickener the settled material contains as much as 40 to 50 pct water. The analysis of the leach solution was as follows: Co, 0.2 to 0.3; Cu, 0.5 to 1.5; Fe, 0.3 to 1.5; Zn, 0.3 to 0.6; Mn, 0.1 to 0.2 g per liter.

Treatment of Solution in General

Recovery of pure cobalt oxide from such a solution is difficult for a variety of reasons. The cobalt concentration is small and any prior removal of copper and iron by any of the usual methods would still leave enough behind to seriously contaminate the cobalt when ultimately recovered. Moreover, extreme dilution made necessary the treatment of such huge quantities of solution that production cost inevitably would be high in the case of a complicated flowsheet involving heating, filtration, reagents, etc. Zinc and manganese are so close to cobalt in chem-

Table X. Comparison of Water and Acid Leaching\*

|                                      | Co, Pct | Cu, Pct | Fe, Pct | Zn, Pct |
|--------------------------------------|---------|---------|---------|---------|
| H <sub>2</sub> O                     | 0.072   | 0.21    | 0.11    | 0.27    |
| 2 pct H <sub>2</sub> SO <sub>4</sub> | 0.076   | 0.35    | 1.10    | 0.39    |

\* Leaching at 80°C for 5 min.

Table XI. Effect of Temperature and Acid Concentration in Leaching\*

| Solvent                                | Temperature,<br>°C | Co, Pct | Cu, Pct | Fe, Pct |
|----------------------------------------|--------------------|---------|---------|---------|
| H <sub>2</sub> O                       | 60                 | 0.069   | 0.15    | 0.08    |
| 0.5 pct H <sub>2</sub> SO <sub>4</sub> | 30                 | 0.070   | 0.19    | 0.32    |
| 0.5 pct H <sub>2</sub> SO <sub>4</sub> | 60                 | 0.068   | 0.23    | 0.78    |
| 2 pct H <sub>2</sub> SO <sub>4</sub>   | 60                 | 0.071   | 0.27    | 1.63    |
| 2 pct H <sub>2</sub> SO <sub>4</sub>   | 90                 | 0.073   | 0.30    | 2.80    |

\* Leaching for 30 min.

Table XII. Effect of Time in Water Leaching\*

| Time, Min | Co, G  | Cu, G  | Fe, G  |
|-----------|--------|--------|--------|
| 5         | 0.0214 | 0.0883 | 0.0200 |
| 10        | 0.0212 | 0.0893 | 0.0211 |
| 20        | 0.0221 | 0.0897 | 0.0266 |
| 40        | 0.0223 | 0.0901 | 0.0191 |

\* 50 g ore was agitated with 100 g water. 50 cc extract analyzed.

Table XIII. Effect of Particle Size on Leaching\*

| Mesh       | Co, Pct | Cu, Pct | Fe, Pct |
|------------|---------|---------|---------|
| + 35       | 0.048   | 0.33    | 0.14    |
| —35 + 65   | 0.055   | 0.33    | 0.15    |
| —65 + 100  | 0.058   | 0.36    | 0.08    |
| —100 + 150 | 0.053   | 0.35    | 0.08    |
| —150 + 200 | 0.050   | 0.31    | 0.11    |

\* Water leaching at 60° for 30 min.

ical behavior that their elimination or separation is difficult even in the case of chemical analysis. No known hydrometallurgical method was entirely satisfactory from a technical and economic viewpoint.

It was decided finally to treat the leach solution to obtain a cobalt precipitate after eliminating only those easily separable elements to such a degree as could be accomplished easily. This means that the solution treatment would be a mere concentrating process differing from the usual hydrometallurgical process in which refining is accomplished.

The simplest operation in each step in the process was chosen; heat was not involved, separation of the bulk of the liquid from any precipitate was by decantation, and the whole was operated continuously so that huge volumes of liquid could be passed through small equipment. Chemical reactions were selected that could be adapted to such a flowsheet. Equipment consisted of small agitation tanks for reagents, one or two medium tanks for completion of reactions, a large Dorr thickener for decantation, and filter presses to take only thickened slurry when necessary. Such cheap and simple steps were arranged for each individual reaction.

### Elimination of Copper and Iron

The simplicity of the equipment referred to above required a precipitate that would settle easily at room temperature, namely one of fairly large particle size. To achieve this in minimum time it was necessary to consider the solubility product of the precipitate to be formed. Copper sulphide or ferric hydroxide, for example, are not suitable because their solubility products are too small to allow the precipitates to coagulate or grow to larger particles. Of course coagulation could be accomplished by applying heat and controlling the pH, but these procedures were out of the question. Since, on the other hand, a high solubility product meant incomplete elimination, there was no alternative but to choose precipitates having a moderate solubility product. In addition the solubility product of the copper or iron precipitate must be low in comparison with that of the cobalt compound present to allow separation. These requirements led to the selection of eliminating copper as the hydroxide.

Regarding the iron, there were many reasons for precipitating it as the hydroxide. Iron was present in the solution as ferrous sulphate. The solubility product of ferric hydroxide was too low, as men-

tioned earlier, and any excess of reagent used for oxidizing ferrous iron is apt to precipitate  $\text{Co}(\text{OH})_2$  together with the iron. Furthermore, ferric hydroxide has a greater tendency to drag down cobalt by occlusion. In the process iron and copper were successfully eliminated simultaneously as  $\text{Fe}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2$ .

Table XVI shows the results of experiments in which varying amounts of soda ash were used for precipitation.

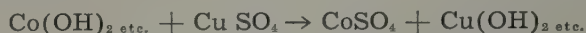
The following comments are important from the standpoint of practical operation:

1—Loss of cobalt is closely related to the excessive elimination of copper from solution.

2—Loss of cobalt increases with increase of iron in the original solution.

3—The elimination of copper and iron must be made in two stages in order to diminish their concentrations below 0.01 g per liter, which means the remaining copper or iron must be less than 1/20th of the cobalt, thus limiting the loss of cobalt to a few percent.

4—The precipitate from the second stage contains considerable cobalt which must be recovered. To do this the thickened slurry is agitated with the original solution in the first agitator where the cobalt is dissolved, Table XVII, according to the following reaction:



This simple method is very effective in saving reagents because the second stage precipitate is not only leached without consuming any particular reagents, but also serves as a base for precipitating copper from the original solution.

Composition of original solution added: Cu 1.05, Co 0.32, Fe 0.05 g per liter. To 100 cc of second copper precipitate slurry, the sulphuric acid or original solution was added, agitated for 30 min at room temperature and filtered. Before treatment 100 cc of second copper precipitate contained the following: Dry material, 1.2 g; Co, 0.024 g; Cu, 0.394 g; and Fe, 0.003 g.

5—Soda ash additions were controlled using the remaining  $\text{CuSO}_4$  in the mother liquor as indicator, 0.1 g per liter in the first stage and 0.01 g per liter in the second. The copper present was determined colorimetrically by the operator. In actual operation

Table XIV. Effect of Grinding on Leaching

| Mesh     | Grinding   | Water Extraction |         |         |
|----------|------------|------------------|---------|---------|
|          |            | Co, Pct          | Cu, Pct | Fe, Pct |
| + 30     | Not ground | 0.030            | 0.11    | 0.03    |
|          | Ground     | 0.030            | 0.10    | 0.10    |
| —30 + 65 | Not ground | 0.027            | 0.13    | 0.05    |
|          | Ground     | 0.030            | 0.12    | 0.07    |
| —65      | Not ground | 0.037            | 0.10    | 0.03    |
|          | Ground     | 0.037            | 0.10    | 0.03    |

Table XV. Comparison of Fresh and Sea Water for Leaching

| Medium          | Co, Pct | Cu, Pct | Fe, Pct |
|-----------------|---------|---------|---------|
| Distilled water | 0.049   | 0.29    | 0.035   |
| Aqueduct water  | 0.049   | 0.29    | 0.029   |
| Sea water       | 0.048   | 0.26    | 0.006   |



the consumption of soda ash was about three times as much in the first stage as in the second.

6—The two-stage elimination of copper and iron was necessary also because, in spite of the large storage tank, the concentration of the feed solution varied considerably, 0.6 to 1.3 g per liter Cu, and with continuous treatment the addition of the correct amount of soda ash was impossible. Therefore, the first addition was purposely somewhat insufficient so that an unexpected decrease of copper in the feed solution would not result in an increase of cobalt in the precipitate. On the other hand, the second soda ash addition was maintained in excess so that a sudden increase of copper would not result in its incomplete elimination.

7—Soda ash was chosen as the precipitant although, from a reagent cost standpoint, milk of lime had some advantage. However, there are some disadvantages in using lime. Calcium sulphate crystallizes on the inner surfaces of pumps, pipes, and tanks making it necessary to use launders for solution transfer and to so place tanks that the transfer can be done by gravity decantation, thus eliminating pumps. Also if there are coarse particles of lime in the reagent there will be excessive precipitation of cobalt in their vicinity. It is preferable to use lime immediately after slaking.

8—The precipitate had the following analysis: Cu, 25 to 35 pct; Fe, 15 to 25 pct; Co, 0.2 to 0.3 pct; and Zn, 2 to 4 pct. This material could be charged into the blast furnace for copper recovery.

Precipitation of Cobalt

Cobalt was precipitated as cobaltic hydroxide using soda ash and chlorine. The chlorine which was purchased as a liquid was introduced into the solution as fine bubbles through porous porcelain tubes. In this process the separation of manganese was difficult since it precipitated as MnO<sub>2</sub> together with the cobalt. Part of the manganese was oxidized to permanganate, coloring the solution. Some zinc is also precipitated along with the cobalt.

Table XVI. Precipitation by Soda Addition\*

| Na <sub>2</sub> CO <sub>3</sub> ,<br>G | Precipitate |           |           |           |           | Filtrate  |           |           |
|----------------------------------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|                                        | Co,<br>Mg   | Cu,<br>Mg | Fe,<br>Mg | Zn,<br>Mg | Mn,<br>Mg | Co,<br>Mg | Cu,<br>Mg | Fe,<br>Mg |
| 0.24                                   | Trace       | 50        | 15        | Trace     | Trace     | 52        | 120       | 28        |
| 0.30                                   | Trace       | 72        | 18        | 1         | Trace     | 53        | 97        | 23        |
| 0.36                                   | Trace       | 98        | 25        | 2         | Trace     | 52        | 71        | 20        |
| 0.42                                   | Trace       | 116       | 27        | 2         | Trace     | 52        | 50        | 15        |
| 0.48                                   | 2.6         | 136       | 35        | 4         | 1         | 49        | 25        | 10        |
| 0.54                                   | 4.8         | 156       | 39        | 16        | 3         | 46        | 10        | 5         |
| 0.60                                   | 8.1         | 155       | 42        | 25        | 5         | 44        | 2         | 3         |

\* Concentration of original solution: Co 0.26, Cu 0.84, Fe 0.22, Zn 0.36, Mn 0.03 g per liter.  
Quantity of original solution: 200 cc.  
Agitated for 1 hr at room temperature.  
Na<sub>2</sub>CO<sub>3</sub> was added as a 10 pct solution.

Table XVII. Dissolution of Cobalt in Second Copper Precipitate

| Addition                              |                           | Residue |       |       | Extract |       |       |
|---------------------------------------|---------------------------|---------|-------|-------|---------|-------|-------|
| H <sub>2</sub> SO <sub>4</sub> ,<br>G | Orig-<br>inal<br>Solution | Co, G   | Cu, G | Fe, G | Co, G   | Cu, G | Fe    |
| 0.2                                   | 0                         | 0.011   | 0.394 | 0.003 | 0.0139  | 0.005 | Trace |
| 0.4                                   | 0                         | 0.0013  | 0.360 | 0.003 | 0.0248  | 0.034 | Trace |
| 0.6                                   | 0                         | 0.0004  | 0.237 | 0.003 | 0.0256  | 0.157 | Trace |
| 0.8                                   | 0                         | 0.0003  | 0.085 | 0.003 | 0.0256  | 0.298 | Trace |
| 0.0                                   | 300 cc                    | 0.0016  | 0.421 | 0.004 | 0.0205  |       |       |

Table XVIII. Standards of Degree of Oxidation and Reduction

|           | Co in<br>Slag, Pct | Mn in<br>Crude Co, Pct |
|-----------|--------------------|------------------------|
| 1st stage | 0.1-0.2            | 3-5                    |
| 2nd stage | 5-10               | 0.1-0.05               |

Table XIX. CoO, MnO Reduction Equilibrium

| Alloy   |         | Slag    |                        |          |
|---------|---------|---------|------------------------|----------|
| Mn, Pct | Co, Pct | Mn, Pct | SiO <sub>2</sub> , Pct | CaO, Pct |
| 5.41    | 0.05    | 11.80   | 25.70                  | 38.09    |
| 3.77    | 0.22    |         |                        |          |
| 1.14    | 0.59    | 31.61   | 37.86                  |          |
| 1.00    | 0.50    | 30.14   | 38.94                  |          |
| 0.57    | 0.67    | 30.79   | 39.94                  |          |
| 0.26    | 1.45    | 32.27   | 37.22                  |          |
| 0.20    | 1.67    | 31.78   | 35.72                  |          |
| 0.07    | 6.29    | 27.52   | 34.66                  |          |

The soda and chlorine additions were so regulated as to maintain a pH of 5.0 to 5.5 and an excess of chlorine, including MnO<sub>2</sub> and ClO<sub>2</sub>, of 0.05 to 0.1 g per liter. The pH was determined with test papers and the free chlorine by simplified permanganometry, both tests being made on the job. Lime cannot be substituted for soda ash in this process since the calcium sulphate thus formed accompanies the cobalt precipitate which in the subsequent reduction process yields cobalt sulphide instead of the desired metallic cobalt. Although the cobalt precipitate obtained was impure the process did serve to produce a concentrate from the dilute leach solution. The analysis of the precipitate was: Co, 30 to 35 pct; Cu, 0.5 to 1.0 pct; Fe, 0.5 to 1.0 pct; Zn, 2 to 8 pct; and Mn, 5 to 8 pct.

Reduction of Cobalt Precipitate

The dried precipitate was mixed with coke breeze and flux and melted in a small electric arc furnace. Crude metallic cobalt containing copper and iron was obtained, the manganese was slagged off, and the zinc was eliminated by vaporization. The crude cobalt containing about 90 pct Co, 2 to 5 pct each of Cu and Fe, 0.5 to 1.5 pct Ni, and traces of Mn and Zn, was refined electrolytically.

In the reduction the chemical similarity of the oxides of cobalt and manganese made it necessary to operate in two stages to eliminate manganese. The first stage was a reducing fusion wherein all of the cobalt and a small amount of the manganese were reduced. The second stage was an oxidizing fusion wherein the manganese was oxidized into the slag by the addition of crude cobalt precipitate. This eliminated the manganese but gave a slag containing cobalt which was recovered by returning the slag to the first stage. The degree of reduction and oxidation in the two stages was adjusted according to the cobalt content of the slag as shown in Table XVIII, based on a study of the equilibrium, Table XIX. The corresponding alloys and slags were obtained by melting CoO, MnO<sub>2</sub>, charcoal, and siliceous sand in various proportions in a crucible over an oxygen-coal gas burner.

Electrolysis

The literature on the electrolytic refining of cobalt is scanty and many details remain to be studied. Nevertheless, pure metallic cobalt was commercially produced by the electrolytic process here described.

The electrolyte was held to about 30 g Co per liter and the sulphate and ammonium ion concentrations regulated to correspond to a nearly equimolecular mixture of cobalt sulphate and cobalt ammonium sulphate. The pH of the solution was maintained at 5.5 after purification, since lower values made it difficult to eliminate iron and higher values gave a

| Period of<br>Operation     | Cinder<br>Treated,<br>Ton | Co<br>Produced,<br>Kg |
|----------------------------|---------------------------|-----------------------|
| September to December 1943 | 7,082                     | 0                     |
| 1944                       | 24,897                    | 6298                  |
| January to August 1945     | 5,413                     | 1373                  |
| Total                      | 37,392                    | 7671                  |

Manganese in the anodes will go into solution where it remains, but zinc will deposit, necessitating complete removal of the latter at the anode furnace.

The pilot plant was operated during 1941 and the commercial plant design was started in 1942. It was decided that the capacity should be 300 tons of pyrite concentrate per day which was the tonnage expected from the Besshi mine. The most serious





Table XXI. Analyses of Intermediate Products (Average)

| Name of Products             | Quantity Treated per Month | Unit | June 1944 |       |       |       |       |       |       |
|------------------------------|----------------------------|------|-----------|-------|-------|-------|-------|-------|-------|
|                              |                            |      | Co        | Cu    | Fe    | Zn    | Mn    | Ni    | S     |
| Pyrite concentrate           | 3025 ton                   | Pct  | 0.10      | 0.28  | 40.76 | 0.37  | 0.03  | Trace | 47.53 |
| Pyrite cinder                | 2180 ton                   | Pct  | 0.14      | 0.41  | 54.20 | 0.11  | 0.04  |       |       |
| Pyrite cinder (soluble part) |                            | Pct  | 0.055     | 0.11  | 0.04  | 0.04  | 0.01  |       |       |
| Leach solution               | 4292 cu m                  | G/L  | 0.22      | 0.69  | 0.19  | 0.10  | 0.02  |       |       |
| Copper precipitate           | 9370 kg                    | Pct  | 0.21      | 25.19 | 13.74 | 2.94  | 0.35  |       |       |
| 2nd copper precipitate       |                            | Pct  | 4.24      | 17.15 | 6.55  | 4.50  | 0.32  |       |       |
| Cobalt precipitate           | 2523 kg                    | Pct  | 36.42     | 0.50  | 0.78  | 2.99  | 5.80  | 0.01  | 2.13  |
| October 1944                 |                            |      |           |       |       |       |       |       |       |
| Cobalt precipitate           | 2674 kg                    | Pct  | 31.66     | 1.00  | 2.40  | 10.65 | 5.83  |       |       |
| Anode                        | 1274                       | Pct  | 88.40     | 2.77  | 4.38  | Trace | 0.24  |       |       |
| Manganese slag               | 912                        | Pct  | 0.26      | 0.07  | 1.88  | 0.20  | 6.58  |       |       |
| Cobalt slag                  | 581                        | Pct  | 9.26      | 0.16  | 5.70  | 0.28  | 6.06  |       |       |
| Zinc oxide dust              | 58                         | Pct  | 2.76      |       |       | 53.81 |       |       |       |
| Pure cobalt                  | 740                        | Pct  | 99.35     | 0.11  | 0.07  | Trace | Trace | 0.26  |       |
| Iron precipitate             | 117                        | Pct  | 15.36     | 0.08  | 22.56 | Trace | 0.45  |       |       |
| Anode slime                  | 114                        | Pct  | 22.66     | 22.10 | 5.51  | Trace | 0.22  |       |       |
| Pure electrolyte             |                            | G/L  | 29.63     | Trace | 0.005 | Trace | 0.56  |       |       |
| Foul electrolyte             |                            | G/L  | 29.60     | Trace | 0.26  | Trace | 0.53  |       |       |

problem was the selection of corrosion resistant materials. Acid was not to be used which helped somewhat, however, the corrosive action of copper sulphate and the erosion by the ore slurry was still a difficult combination to overcome. Cupro-nickel or 18-8 stainless steel were best suited, but they were in scarce supply. Consequently tanks, pipes, and air lift pumps were made of reinforced concrete. A few parts including an air nozzle were made of 13 pct Cr steel. Launderers and agitator were made of wood, and pumps were of bronze or hard lead. All equipment except the roasting furnace was made on the job. Construction started in August 1942 and was completed in August 1943 at a cost of about 1,000,000 yen. Arrangement of the main equipment is indicated in Fig. 1.

### Commercial Operation

The operation was started in September 1943 and continued successfully until the surrender in 1945. The quantities treated and produced and some examples of analyses of raw material, intermediate and final products are shown in Tables XX and XXI.

### Economics

The project was demanded by the war economy regardless of cost, but it represents a sincere effort on the part of the author to develop a process which would be profitable even in peace time. Indeed the operating cost under normal conditions estimated from the actual results show a cost less than the prewar price of cobalt. However, the actual cost calculated from the data of the short operating period was high owing to the high repair costs incurred by the small but numerous faults of the equipment in the early days of operation. In fact, the process was profitable even during the war in comparison with other plants in Japan upon whose costs the controlled price of cobalt was based. Further reduction in cost is anticipated by substituting milk of lime for most of the soda ash which is responsible for a large part of the cost, or by replacing chlorine and soda ash for cobalt precipitation with bleach solution produced by direct electrolysis of sea water.

### Summary

Metallic cobalt was obtained from cupriferous pyrite as a byproduct of copper production at Besshi

mine and smelter, Japan. The project was undertaken because, since the early thirties, it was necessary for Japan to be self-sufficient in cobalt. The research work started in 1939 and was finished in 1940. The pilot plant was operated in 1941 and the final plant produced cobalt from 1943 until the Japanese surrender in 1945. About 7 tons of metallic cobalt were produced from approximately 37,000 tons of pyrite cinder.

Owing to the extremely low grade of the ore (0.1 pct Co) it was difficult to make the project profitable, however this was accomplished by the process which is summarized as follows:

1—Iron pyrite concentrate, obtained as froth from the flotation mill after separating chalcopyrite, was treated for cobalt production. It was roasted for sulphuric acid production and then leached.

2—The leach solution, containing  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{ZnSO}_4$ , and  $\text{MnSO}_4$ , in addition to  $\text{CoSO}_4$ , was treated by a simple process to obtain a crude cobalt precipitate after a rough elimination of copper and iron. A complete refining of cobalt was not intended because of the expense of treating large quantities of solution by a complicated procedure.

3—Crude metallic cobalt was obtained from the precipitate by a reducing fusion which eliminated zinc and manganese whose removal would otherwise have been difficult.

4—The crude metallic cobalt was refined by electrolysis.

5—Because of shortages of construction material the whole process was designed to use few units of simple design and special stress was laid on this requirement during development.

### Acknowledgment

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# Effects of Precompression On The Behavior of the Aluminum Alloy 24ST4 During Cyclic Direct Stressing

by S. I. Liu

THE effects of strain histories, consisting of several prestrains in opposite directions, on the flow and fracturing characteristics of metals determined in a final test have been investigated previously.<sup>1-3</sup> Such strain histories vary from a single prestrain in tension or compression to the number of strain cycles leading to fatigue failure.<sup>1</sup> Between these two limits, various strain histories could be visualized and some can be attained readily. One such example is a strain history consisting of a first prestrain in tension of various magnitudes and a second prestrain in compression also of various magnitudes.<sup>2</sup> In this investigation the strain history was extended to the combination of these two limits, i.e., a single prestrain in tension or compression followed by balanced strain cycles of a selected magnitude  $\epsilon_0 = \pm 0.12$ . It was found in this case that only compressive initial prestrains could be investigated with sufficient accuracy.\*

Such strain histories can be considered also as (low cycle) fatigue tests of a metal subjected to various amounts of cold working. It appears from previous publications that cold working within a wide range of reductions usually raises the unnotched fatigue strength of many metals.<sup>4-6</sup> This effect, however, has been found to be inconsistent and sometimes reversed for other metals.<sup>5,7</sup> Furthermore, Ludwik reports that the yield strength of cold-worked specimens may be reduced by cyclic strains, while that of materials without cold work is generally increased in the initial cycles.<sup>8,9</sup>

In addition to the above tests, a study was made of the effect of intermediate re-solution heat treatment on low cycle fatigue behavior. Such anneals should eliminate the strain hardening induced by the cyclic strains. As far as their effect on the fracture characteristics is concerned, a few previous tests seemed to indicate that the damage resulting from cyclic strains is retained only partially after heat treatment.<sup>10</sup>

A further investigation was made in which one specimen was subjected to repeated unbalanced tension cycles in which the strain interval was approximately  $+0.013$ . This repetition of plastic tension

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Fig. 1 (right)—Test specimen for cyclic loading.

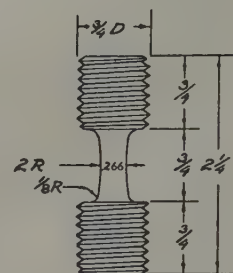
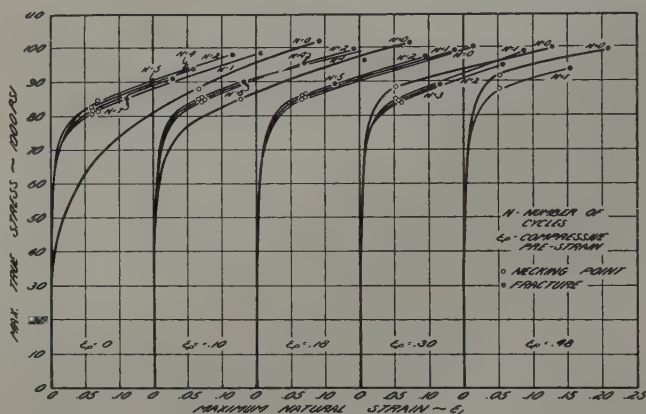


Fig. 2 (below)—Stress-strain curves for the precompressed aluminum alloy 24ST4 after various strain cycles at a strain of  $\epsilon_0 = \pm 0.12$ .



damages the material slightly. This result appears to confirm Ludwik's observations.<sup>8,9</sup>

Commercial  $3/4$ -in. rod of the aluminum alloy 24ST4 was selected for this investigation. The material was subjected to the following treatments before machining: 1—Re-solution treatment at  $920^\circ \pm 10^\circ\text{F}$  for 45 min, 2—water quench at room temperature, and 3—aging for four days at room temperature.<sup>†</sup> The treated material then was machined to desired specimen contour and tested. A coolant was used during machining to minimize any artificial aging effects of heating during machining. In some cases the 24ST4 specimens were reheat treated after having been strained. In these cases, the heat treatment was the same as the re-solution heat treatment described above.

## Procedure

As shown in Fig. 1, threaded end specimens with a minimum diameter of 0.266 in. and a contour radius of 2 in. were used for prestraining to an axial compressive strain ranging from  $\epsilon_p = -0.10$  to  $\epsilon_p = -0.48$ . For large prestrains, two consecutive com-

\* After a comparatively large initial tension and machining, necking no longer took place at the original minimum section.

† This alloy reportedly is stable as regards mechanical properties after a natural aging period of four days.



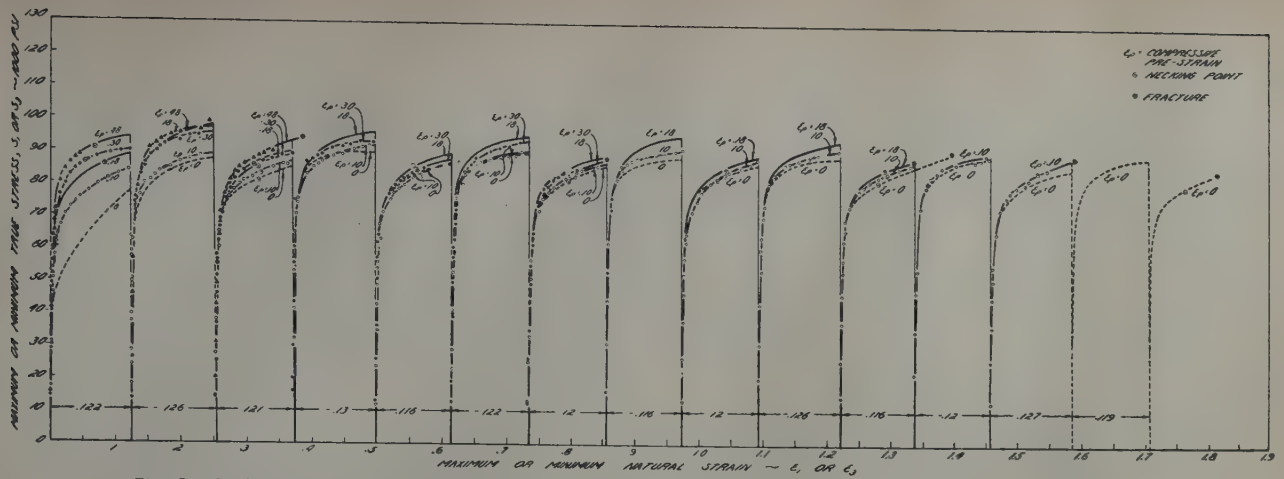


Fig. 3—Cyclic stress-strain characteristics of the aluminum alloy 24ST4 after various amounts of precompression.

pressions with an intermediate machining were applied, the amount of compressive strain performed in each single compression being kept below  $\epsilon_p = -0.30$  to avoid buckling. The precompressed specimen was machined to its initial contour and finally subjected to cyclic straining. Each strain cycle consisted of a first strain in tension  $\epsilon_1 = +0.12$  and a second strain in compression  $\epsilon_2 = -0.12$ . Such tension-compression strain cycles were carried on until fracture took place. To investigate the progressive change in fracturing characteristics, specimens were subjected to failure in tension after various numbers of cycles. As was pointed out before, no significant change in specimen contour was observed after each cycle.

The prestrains, the strain cycles, and the final testing all were done on a regular hydraulic 60,000-lb tensile machine. Concentricity during compression

was obtained by using a truncated-cone-shaped fixture attached to an antifriction die set and concentricity during tension, by using a specially designed fixture.<sup>11</sup> The change of diameter at the minimum section in either tension or compression was measured by means of a radial strain gage which measured changes in diameter directly to 0.0001 in.<sup>2</sup> The stress-strain relations for all strain cycles and all final tests thus obtained are presented in Figs. 2 to 12.

## Results

**Effects of Precompression on the Flow Characteristics during Cyclic Loading:** The changes in flow characteristics are illustrated in Figs. 2 to 5. Each family of curves in Fig. 2 corresponds to a given value of precompression, and each family consists of stress-strain curves obtained on specimens tested after various numbers of strain cycles. In Fig. 3, stress-strain curves for each given value of precompression were plotted in the sequence of straining, regardless of the difference in the signs of stresses and strains. In Fig. 4, each family of curves corresponds to a given number of cycles, and each family consists of stress-strain curves from specimens strained to various values of precompression before the given number of cycles. The stress required to perform the selected value of strain ( $\pm 0.12$ ), the true necking stress, and the conventional tensile strength are plotted in Figs. 5a and b, as functions of the number of cycles.

From Figs. 2 to 5, the following can be deduced regarding the effects of precompression on the flow characteristics:

1—Cyclic straining of a re-solution heat treated metal apparently creates two superimposed and counteracting effects; namely, strain hardening and deterioration. For a given magnitude of cyclic strain, strain hardening disappears after a certain number of cycles, while the deteriorating effect continues until a fatigue-type fracture takes place. As shown in Fig. 2, for the selected value of cyclic strain ( $\epsilon_0 = \pm 0.12$ ) the net effect of the first cycle could be either strain hardening or deterioration, depending upon the magnitude of the precompression. For small precompressions between 0.00 and  $-0.18$ , the effect of the first cycle is strain hardening and the amount of strain hardening decreases with increasing precompression; on the contrary, for large compressions between  $-0.3$  and  $-0.48$ , the net effect of the first cycle is deterioration as shown by the lowered stress-strain curves after the first cycle.

2—As shown in Figs. 3 and 4, as the number of

## Symbols

|                                      |                                                                                                                                                                                                                |
|--------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Cyclic strain $\epsilon_0$           | = Either one of two limits of natural strain in a balanced strain cycle consisting of a first strain $\epsilon_1$ in tension and a second strain in compression $\epsilon_2$ , ( $\epsilon_2 = -\epsilon_1$ ). |
| Prestrain $\epsilon_p$               | = Prestrain in either tension (positive) or compression (negative).                                                                                                                                            |
| Fracture stress $S_f$                | = Load at fracture divided by the area at the minimum section at the moment of fracture.                                                                                                                       |
| Retained ductility $\epsilon_f$      | = Maximum natural strain after fracture.                                                                                                                                                                       |
| Number of cycles $N$                 | = Number of repetitions of strain cycles.                                                                                                                                                                      |
| Changes in fracture stress $(S_f)_n$ | = Change in fracture stress due to precompression only ( $n = \text{constant}$ ).                                                                                                                              |
| $(S_f)_p$                            | = Change in fracture stress due to strain cycles only ( $\epsilon_p = \text{constant}$ ).                                                                                                                      |
| Changes in retained ductility:       |                                                                                                                                                                                                                |
| $(\epsilon_f)_n$                     | = Change in retained ductility due to precompression only ( $n = \text{constant}$ ).                                                                                                                           |
| $(\epsilon_f)_p$                     | = Change in retained ductility due to strain cycles only ( $\epsilon_p = \text{constant}$ ).                                                                                                                   |

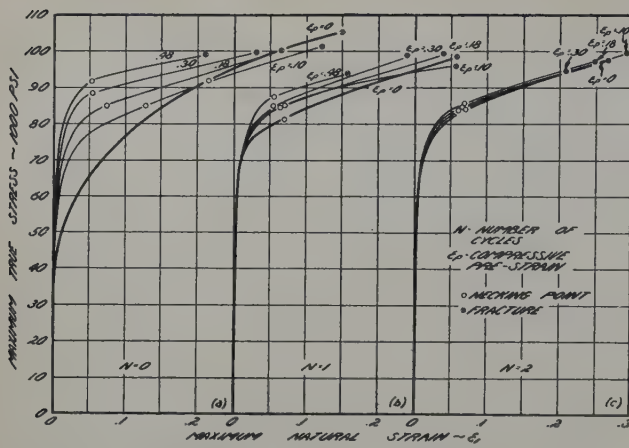
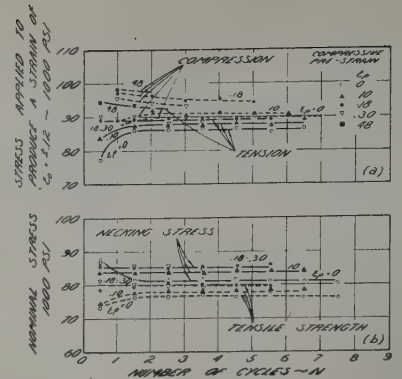


Fig. 4 (left)—Stress-strain curves for the precompressed aluminum alloy 24ST4 after various strain cycles at a strain of  $\epsilon_0 = \pm 0.12$ .

Fig. 5 (right)—Effect of precompression on the flow characteristics of the aluminum alloy 24-ST4 under cyclic straining at a strain of  $\epsilon_0 = \pm 0.12$ .



straining cycles increases, the stress-strain curves for various magnitudes of precompression approach each other. Moreover, a reversal of the order of strain hardening takes place after two cycles, i.e., the stress-strain curves after the first several cycles become lower than those of the first several cycles. These appear to be the results of the counteraction between strain hardening and deterioration.

3—As shown in Fig. 5, the stresses required to perform the desired cyclic strain, the necking stress, and the tensile strength all remain constant after the first cycle. The yield strength after large precompressions decreases slightly with increasing number of cycles.

**Effects of Precompression on the Fracturing Characteristics under Cyclic Straining:** The total strain history introduced in this investigation consisted of two parts: The precompression and the following strain cycles. In order to visualize the combined effects of both on the fracturing characteristics of the material, the individual effect of each part should be considered. Thus the following four quantities were introduced here for graphical representation of experimental results:

$(\epsilon_f)_n (S_f)_n$  = change in ductility and fracture stress due to precompression only ( $n$  = constant)

$(\epsilon_f)_p (S_f)_p$  = change in ductility and fracture stress due to strain cycles only ( $\epsilon_p$  = constant)

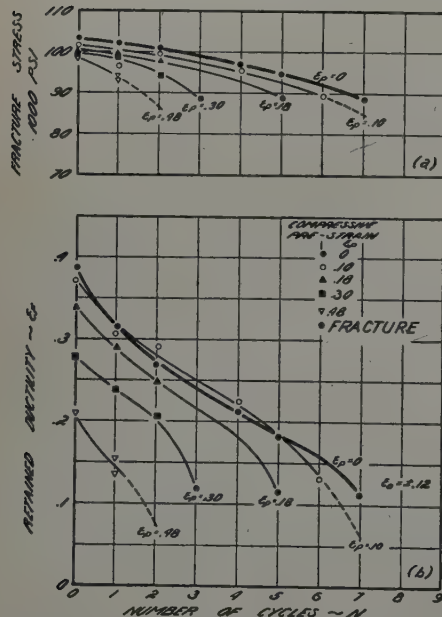
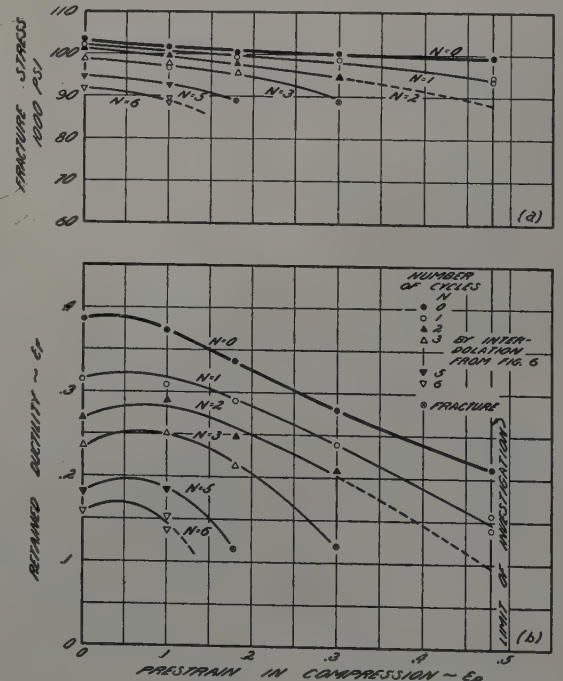


Fig. 6 (left)—Effect of strain cycles ( $\epsilon_0 = \pm 0.12$ ) on the fracturing characteristics of the aluminum alloy 24ST4 after various amounts of compressive prestrain.

Fig. 7 (right)—Effect of precompression on the fracturing characteristics of the aluminum alloy 24ST4 under cyclic straining at a strain of  $\epsilon_0 = \pm 0.12$ .





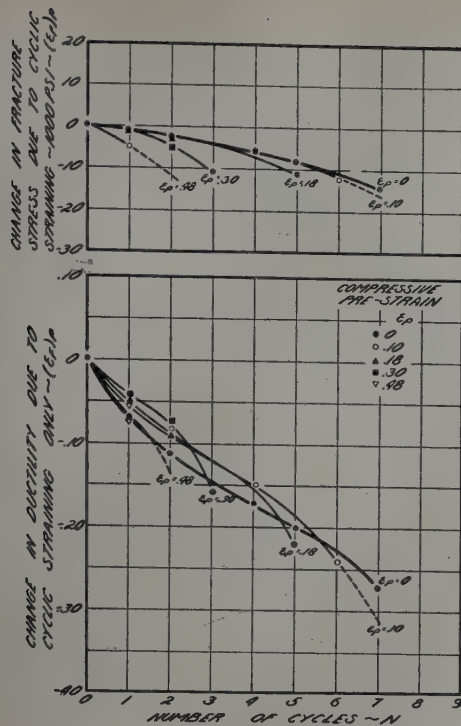


Fig. 8 (left)—Change in fracturing characteristics of precompressed aluminum alloy 24ST4 due to cyclic straining ( $\epsilon_0 = \pm 0.12$ ) as functions of the number of cycles.

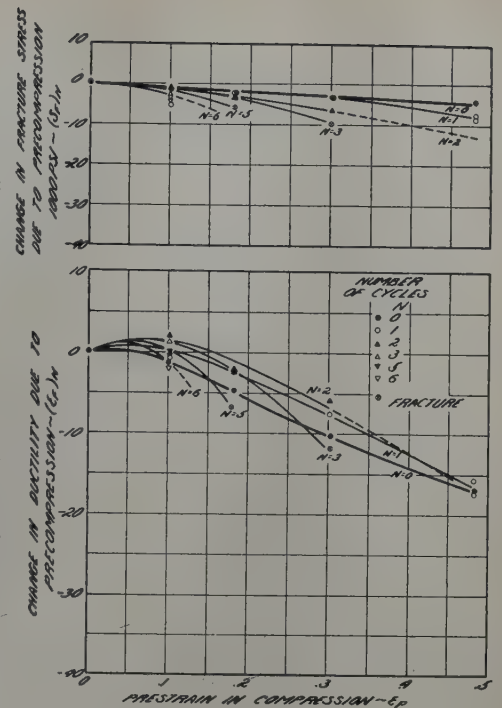


Fig. 9 (right)—Change in fracture characteristics of the cyclically strained aluminum alloy 24ST4 ( $\epsilon_0 = \pm 0.12$ ) due to precompression as functions of the precompression.

precompression was increased by inserted strain cycles as shown in Fig. 9a.

Thus it appears that within the range of precompression and number of cycles investigated, each of these two factors, precompression and cyclic straining, causes a reduction in fracture stress of the material when acting alone; on the other hand, when acting together, the combined effect appears greater than the sum of the two individual effects.

3—The effects of precompression on the retained ductility after varying numbers of strain cycles were as follows:

(a) For precompressions at magnitudes greater than 0.10, the ductility of the virgin material was decreased with increasing precompression as shown in Fig. 6b and 7b.

(b) As shown in Fig. 6b, and the previous investigation,<sup>1</sup> the ductility of the material was decreased suddenly between the last cycle and the fatigue fracture. Fig. 8b shows that precompression increases the rate of such reduction in ductility and accelerates the approach of such a sudden reduction, i.e., accelerates the occurrence of fracture. However, the test data also show that except in the last cycle, the rate of reduction in ductility by cyclic straining was decreased by precompression.

4—The effects of strain cycles inserted between precompression and the final testing on the retained ductility for varying precompression were:

(a) The ductility of the virgin material was decreased with the increasing number of strain cycles as shown in Fig. 6b and 7b.

(b) The rate of change in ductility due to precompression was changed with the increasing number of inserted strain cycles. As shown in Fig. 9b for precompressions of magnitude greater than 0.10, the rate of reduction in ductility by precompression increases with increasing number of cycles.

Previous investigations showed that cold working in drawing or rolling up to very high reduction usually increased the unnotched strength of metals.<sup>4-6</sup>

This investigation, however, indicates that the effect of precompression is opposite to the effect of drawing or rolling. It previously was found in this laboratory and also by other authors, that prestrain in drawing or rolling increases, while prestrain in compression decreases, the fracture stress of many metals in the subsequent tensile test.<sup>3</sup> This finding appears to be in good agreement with the results of this investigation.

Effects of Intermediate Reheat Treatment† on Low Cycle Fatigue Behavior: Fig. 10 shows the stress-strain curves in tension up to fracture after different numbers of cycles, for specimens without intermediate re-solution heat treatment, specimens with intermediate re-solution heat treatment after each cycle, and specimens with only one re-solution heat treatment before the final testing. In this case, no precompression was used. The figure shows that even after re-solution heat treatment, the stress-

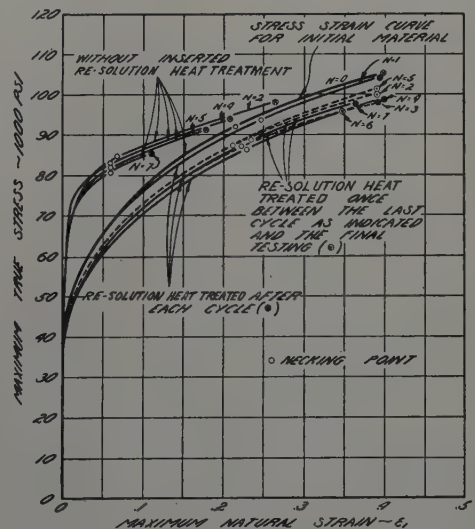


Fig. 10—Stress-strain curves for the aluminum alloy 24ST4 after cyclic straining at a strain of  $\epsilon_0 = \pm 0.12$  with and without inserted re-solution heat treatment, showing the permanent damage done by cyclic straining.

† In this series, the reheat treatment consisted of the regular solution heat treatment and natural aging described earlier in this paper.

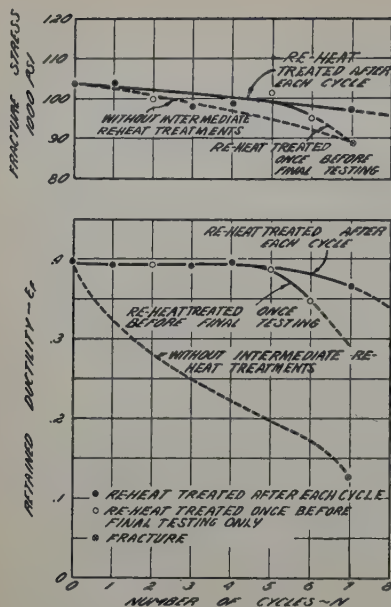
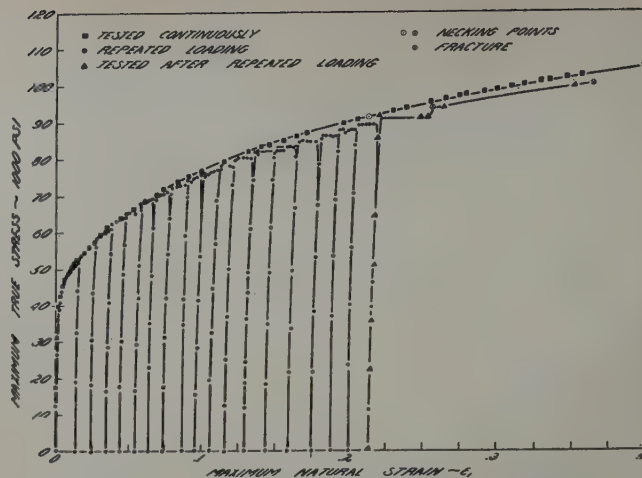


Fig. 11 (left)—Fracturing characteristics of the aluminum alloy 24ST4 under cyclic straining at a strain of  $\epsilon_0 = \pm 0.12$  with and without intermediate reheat treatment, showing the permanent damage done by cyclic loading.

Fig. 12 (right)—Effect of repeated plastic tension on flow and fracture characteristics of the aluminum alloy 24ST4.



greater than the sum of two individual effects, Fig. 8.

3—Within the range of precompression and the number of cycles investigated, precompression accelerates the approach of fracture, Fig. 6.

4—Cyclic straining permanently damages the material, Figs. 10 and 11.

5—A pronounced yield jog appears after repeated tension cycles, and the flow and fracturing characteristics are slightly lowered, Fig. 12. This yield jog is not present in the virgin unstrained metal.

### Acknowledgments

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strain curves of the cyclically strained material are lower than the stress-strain curve of the virgin material.

In Fig. 11, the fracturing characteristics for specimens with and without inserted reheat treatment were plotted as functions of the number of cycles. This figure reveals that after a certain definite number of cycles, five in this case, the ductility of the cyclically strained material can no longer be restored to the value of the virgin material, regardless of the number of intermediate reheat treatments. However, at higher number of cycles, the amount restored by successive reheat treatment after each cycle is larger than that restored by a single reheat treatment before the final testing.

These all point to one fact, that the metal was damaged permanently by cyclic straining. This appeared to confirm the previous findings.<sup>10</sup>

**Stress-strain Curves for 24ST4 in Repeated Tension:** Fig. 12 shows the stress-strain curves for two specimens of the same material, one tested in tension continuously and the other subjected to 19 strain repetitions at a strain interval of approximately 0.01 and tested to fracture. Such repetitions of small plastic strains caused the following changes in the stress-strain behavior of this material: 1—Both the flow and the fracturing characteristics were slightly lowered. 2—A pronounced yield jog which the virgin material does not possess appeared after a number of repetitions.

Such slight reduction in both flow and fracturing characteristics is due apparently to the damages done by repeated loading.

### Conclusions

The experimental results lead to the following conclusions regarding this investigation:

1—Cyclic straining of re-solution heat treated 24ST4 creates two superimposed and counteracting effects, namely, strain hardening and deterioration. After small amounts of precompression, strain hardening prevails during the first few cycles, while after large precompression, deterioration prevails from the first cycle, Fig. 2.

2—When acting alone, either of the two factors, precompression or cyclic straining, causes a reduction in fracture stress of this material; on the other hand, when acting together, the combined effect is



# Effect of Alloying Elements on The Electrical Resistivity of Aluminum Alloys

by A. T. Robinson and J. E. Dorn

The electrical resistivities of aluminum alloys containing Cu, Ge, Zn, Ag, Cd, and Mg were found to increase linearly with the atomic percentage of the solute atoms. Application of Linde's rule to these data suggests that each aluminum atom contributes 2.5 electrons to the metallic bond.

**A**LTHOUGH aluminum invariably exhibits a valence of three in ionic solids, it does not follow necessarily that its valence in the metallic state is also three. As a matter of record, many properties suggest that the number of bonding electrons in metallic aluminum is less than three. For example, as shown in Fig. 1, the atomic radii<sup>1</sup> of the metallic elements in the solid state decrease with increasing atomic number at the beginning of any one period. The atomic radius of aluminum, however, is greater than that which would result from a regular decrease in atomic radius with increasing atomic number, suggesting that the number of bonding electrons in aluminum is somewhat less than three.

Correlated with the anomalously large atomic radius of aluminum is its abnormally low melting temperature. As the atomic numbers increase in any one period, the melting temperatures of the metallic elements increase.<sup>2</sup> As shown in Fig. 2, however, the melting temperature of aluminum (13) is only slightly greater than that of magnesium (12). Again the number of bonding electrons in metallic aluminum appears to be nearer two than the expected value of three.

In addition Ageev and Ageeva<sup>3</sup> calculated the electron density distribution in the aluminum lattice. A comparison of such electron density curves for various assumed valence states of aluminum

with experimentally determined curves suggests that the actual number of bonding electrons in metallic aluminum is between two and three. Hume-Rothery and Raynor<sup>4,5</sup> have suggested that the above-mentioned abnormalities are associated with the overlapping of the Brillouin zones of metallic aluminum when it is in the usual face-centered cubic structure.

The importance of the number of bonding electrons in metals has been extended recently into the field of mechanical properties. While formerly it was thought that the plastic properties of alpha solid solutions were primarily dependent upon the lattice strain induced in the solvent by the solute, it is now known that the difference in the number of bonding electrons of the solute and solvent also has its influence on the plastic properties.<sup>6,7</sup> In order to achieve a satisfactory correlation of the effect of alloying elements on the plastic properties of aluminum alloys,<sup>6,7</sup> however, it was necessary to assume that the number of bonding electrons contributed by aluminum was about two rather than the expected value of three. It appeared to be desirable, therefore, to seek other criteria for evaluating the number of bonding electrons contributed by aluminum to its alpha solid solutions, especially in view of the practical as well as the theoretical importance of the effect of valency on the plastic properties.

Norbury<sup>8</sup> was perhaps the first to illustrate that the increase in resistance of alpha solid solutions is associated with the differences in valence of the solute and solvent metals. In a series of illuminating investigations Linde<sup>9-11</sup> has shown that the electrical

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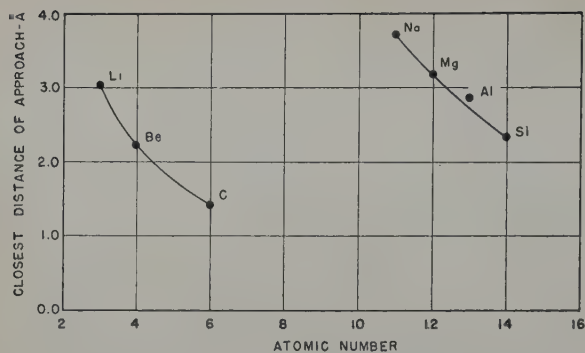


Fig. 1 (above)—Variation of interatomic distances with atomic number. Data from Metals Handbook.

Fig. 2 (below)—Variation of melting temperatures with atomic number. Data from Metals Handbook.

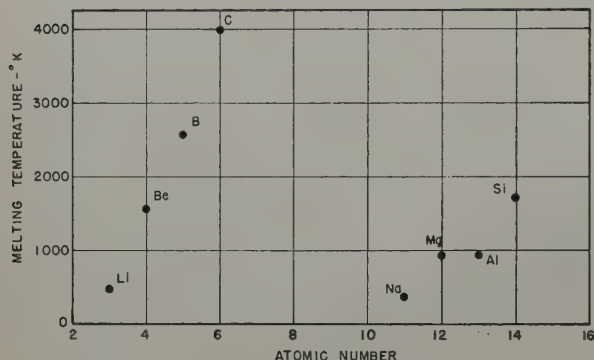


Table I. Equation Constants Used for the Calculated Change in Resistance of Copper, Silver, and Gold Alloys

| Element       | Atomic Number | $Z_\beta$     | $k_1$  | $k_2$  |
|---------------|---------------|---------------|--------|--------|
| <b>Copper</b> |               |               |        |        |
| Cu            | 29            | (1) $_\alpha$ |        |        |
| Zn            | 30            | 2             | 0.4175 | 0      |
| Ga            | 31            | 3             | 0.4175 | 0      |
| Ge            | 32            | 4             | 0.4175 | 0      |
| As            | 33            | 5             | 0.4175 | 0      |
| Ag            | 47            | 1             | 0.322  | 0.1172 |
| Cd            | 48            | 2             | 0.322  | 0.1172 |
| In            | 49            | 3             | 0.322  | 0.1172 |
| Sn            | 50            | 4             | 0.322  | 0.1172 |
| Sb            | 51            | 5             | 0.322  | 0.1172 |
| Au            | 79            | 1             | 0.478  | 0.522  |
| Hg            | 80            | 2             | 0.478  | 0.522  |
| <b>Silver</b> |               |               |        |        |
| Cu            | 29            | 1             | 0.536  | 0.0683 |
| Zn            | 30            | 2             | 0.536  | 0.0683 |
| Ga            | 31            | 3             | 0.536  | 0.0683 |
| Ge            | 32            | 4             | 0.536  | 0.0683 |
| As            | 33            | 5             | 0.536  | 0.0683 |
| Ag            | 47            | (1) $_\alpha$ |        |        |
| Cd            | 48            | 2             | 0.456  | 0      |
| In            | 49            | 3             | 0.456  | 0      |
| Sn            | 50            | 4             | 0.456  | 0      |
| Sb            | 51            | 5             | 0.456  | 0      |
| Au            | 79            | 1             | 0.437  | 0.358  |
| Hg            | 80            | 2             | 0.437  | 0.358  |
| Ti            | 81            | 3             | 0.437  | 0.358  |
| Pb            | 82            | 4             | 0.437  | 0.358  |
| Bi            | 83            | 5             | 0.437  | 0.358  |
| <b>Gold</b>   |               |               |        |        |
| Cu            | 29            | 1             | 0.488  | 0.4403 |
| Zn            | 30            | 2             | 0.488  | 0.4403 |
| Ga            | 31            | 3             | 0.488  | 0.4403 |
| Ge            | 32            | 4             | 0.488  | 0.4403 |
| Ag            | 47            | 1             | 0.3214 | 0.314  |
| Cd            | 48            | 2             | 0.3214 | 0.314  |
| In            | 49            | 3             | 0.3214 | 0.314  |
| Sn            | 50            | 4             | 0.3214 | 0.314  |
| Au            | 79            | (1) $_\alpha$ |        |        |
| Hg            | 80            | 2             | 0.3914 | 0      |

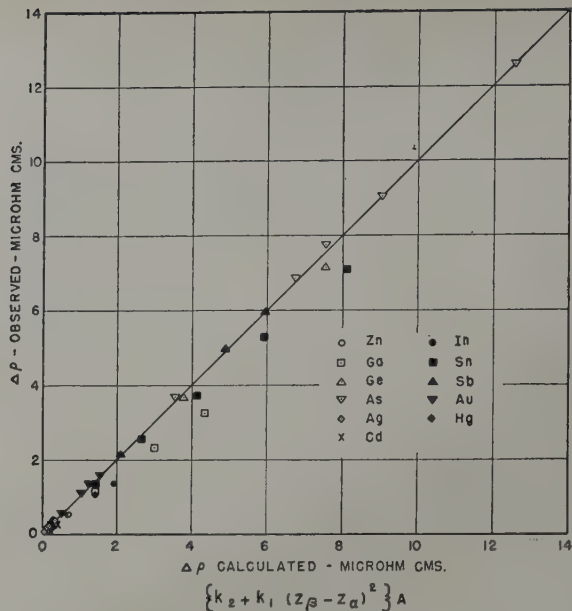


Fig. 3—Agreement between calculated and observed resistance of various solid solution alloys of copper.

resistivity of alpha solid solutions in copper, silver, and gold closely obey the empirical relationship:

$$\Delta \rho = \{k_2 + k_1 (Z_\beta - Z_\alpha)^2\} A \quad [1]$$

where  $A$  is the atomic pct of the solute,  $Z_\alpha$  is the valence of the solvent,  $Z_\beta$  is the valence of the solute,  $\Delta \rho$  is the increase in resistivity per addition of  $A$ , and  $k_1$  and  $k_2$  are constants for any one period from which the solutes are selected.

The validity of the above relationship for alloys of copper is illustrated in Fig. 3 where the observed  $\Delta \rho$  is plotted as a function of the calculated  $\Delta \rho$  using the values of  $k_1$  and  $k_2$  given in Table I. In Figs. 4 and 5 are shown the validity of eq 1 for silver and for gold alloys using the data of Table I. The good agreement between  $\Delta \rho$  observed and  $\Delta \rho$  calculated reveals that eq 1 is quite accurate for the alloy systems which have been investigated.

It has been shown by Mott<sup>12, 13</sup> that the results of Linde as expressed by eq 1 have, in part, a simple theoretical explanation: The core of the solvent atom has a charge of  $Z_\alpha e$  whereas the core of the dissolved atom carries a charge of  $Z_\beta e$  which differs by  $(Z_\beta - Z_\alpha) e$  from that of the solvent. But since the intensity of the scattering of the conduction electrons is proportional to the square of the scattering charge, the change in resistivity should be proportional to  $(Z_\beta - Z_\alpha)^2$  when other factors are neglected.

In view of the above evidence, it should be possible, by application of eq 1 to alpha solid solutions of aluminum, to deduce the value of  $Z_\alpha$ , namely the charge on the core of the aluminum ions in metallic aluminum.

### Materials for Investigation

The alloys examined in this investigation were the same as those previously used for the determination of the effect of alloying elements on the plastic properties of aluminum.<sup>6, 7</sup> Their chemical analyses and their lattice constants are recorded in Table II. Each alloy was homogenized, cold rolled, and re-



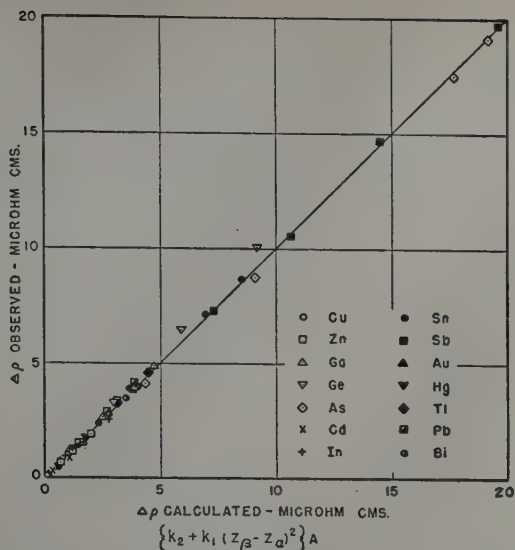


Fig. 4 (above)—Agreement between calculated and observed resistance of various solid solution alloys of silver.

Fig. 5 (below)—Agreement between calculated and observed resistance of various solid solution alloys of gold.

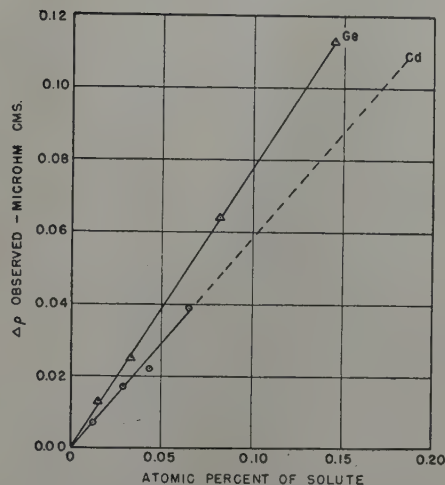
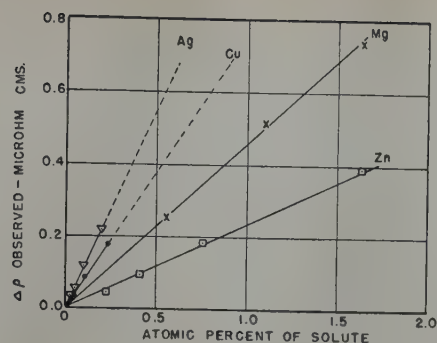
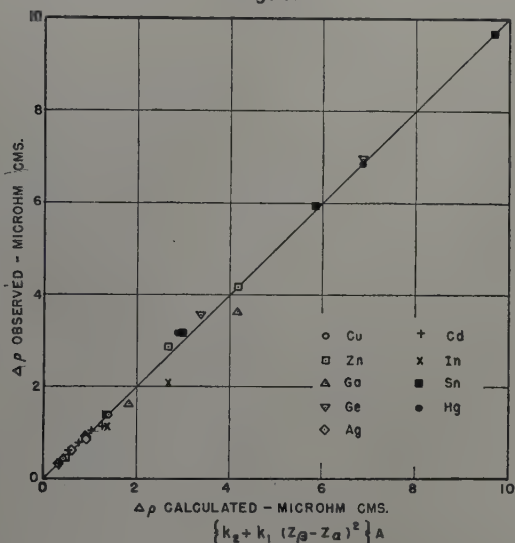


Fig. 6—Effect of alloying elements on the resistance of aluminum.

crystallized to approximately uniform grain size preliminary to the determination of the resistivity.

### Experimental Procedure

Sheet-type specimens having nominal dimensions of 0.070 in. thick and 0.250 in. wide were used in this investigation. Their resistance was determined by means of a precision Kelvin double bridge ohmmeter, the specimen length between the potential leads of the Kelvin bridge being fixed at 2.750 in. The width and thickness of the specimens were measured at three points along their length by means of a vernier micrometer with a least count of 0.0001 in. The errors in the resistivity resulting from errors in gaging the specimen were determined

Table II. Chemical Analyses and Lattice Constants

| Alloying Element | Atomic Pct | kx Units 25°C Lattice Atomic Constant | No. | Residual Impurities, Wt Pct |       |       |        |       |
|------------------|------------|---------------------------------------|-----|-----------------------------|-------|-------|--------|-------|
|                  |            |                                       |     | Si                          | Fe    | Cu    | Mg     | Mn    |
| Mg               | 0.554      | 4.0432(6)                             | 12  | 0.003                       | 0.003 | 0.007 |        |       |
|                  | 1.097      | 4.0454(5)                             |     | 0.004                       | 0.004 | 0.007 |        |       |
|                  | 1.617      | 4.0474(9)                             |     | 0.003                       | 0.004 | 0.006 |        |       |
| Cu               | 0.029      | 4.0411(0)                             | 29  | 0.003                       | 0.004 |       | 0.0006 | 0.001 |
|                  | 0.054      | 4.0408(7)                             |     | 0.003                       | 0.004 |       | 0.0007 | 0.001 |
|                  | 0.101      | 4.0406(9)                             |     | 0.003                       | 0.003 |       | 0.0006 | 0.001 |
|                  | 0.233      | 4.0403(8)                             |     | 0.003                       | 0.004 |       | 0.0006 | 0.001 |
| Zn               | 0.211      | 4.0411(3)                             | 30  | 0.004                       | 0.004 | 0.006 | 0.001  |       |
|                  | 0.402      | 4.0409(8)                             |     | 0.004                       | 0.005 | 0.006 | 0.001  |       |
|                  | 0.755      | 4.0407(1)                             |     | 0.004                       | 0.005 | 0.006 | 0.001  |       |
|                  | 1.616      | 4.0402(0)                             |     | 0.003                       | 0.005 | 0.007 | 0.001  |       |
| Ge               | 0.015      | 4.0413(0)                             | 32  | 0.004                       | 0.004 | 0.006 | 0.001  |       |
|                  | 0.033      | 4.0413(5)                             |     | 0.004                       | 0.004 | 0.006 | 0.001  |       |
|                  | 0.082      | 4.0413(9)                             |     | 0.003                       | 0.005 | 0.007 | 0.001  |       |
|                  | 0.145      | 4.0414(9)                             |     | 0.003                       | 0.006 | 0.007 | 0.001  |       |
| Ag               | 0.025      | 4.0412(8)                             | 47  | 0.003                       | 0.005 | 0.006 | 0.001  |       |
|                  | 0.053      | 4.0412(9)                             |     | 0.003                       | 0.005 | 0.006 | 0.001  |       |
|                  | 0.100      | 4.0413(1)                             |     | 0.003                       | 0.005 | 0.007 | 0.001  |       |
|                  | 0.194      | 4.0413(1)                             |     | 0.003                       | 0.006 | 0.007 | 0.001  |       |
| Cd               | 0.012      | 4.0411(6)                             | 48  | 0.004                       | 0.005 | 0.006 | 0.001  |       |
|                  | 0.029      | 4.0411(0)                             |     | 0.004                       | 0.005 | 0.006 | 0.001  |       |
|                  | 0.043      | 4.0410(6)                             |     | 0.004                       | 0.005 | 0.006 | 0.001  |       |
|                  | 0.065      | 4.0410(6)                             |     | 0.004                       | 0.005 | 0.006 | 0.001  |       |

Table III. Effect of Alloying Elements on the Electrical Resistance of Aluminum, Measured Values

| Alloy | Atomic Pct | ρ Avg Microhm Cm | Δρ Microhm Cm |
|-------|------------|------------------|---------------|
| Mg    | 0.554      | 3.030            | 0.250         |
|       | 1.097      | 3.296            | 0.516         |
|       | 1.617      | 3.520            | 0.740         |
| Cu    | 0.029      | 2.732            | 0.021         |
|       | 0.054      | 2.747            | 0.036         |
|       | 0.101      | 2.793            | 0.082         |
| Zn    | 0.233      | 2.889            | 0.178         |
|       | 0.211      | 2.764            | 0.044         |
|       | 0.402      | 2.811            | 0.091         |
| Ge    | 0.755      | 2.902            | 0.182         |
|       | 1.616      | 3.110            | 0.390         |
|       | 0.015      | 2.760            | 0.013         |
| Ag    | 0.033      | 2.772            | 0.025         |
|       | 0.082      | 2.811            | 0.064         |
|       | 0.145      | 2.860            | 0.113         |
| Cd    | 0.025      | 2.755            | 0.033         |
|       | 0.053      | 2.775            | 0.053         |
|       | 0.100      | 2.838            | 0.116         |
|       | 0.194      | 2.939            | 0.217         |
|       | 0.012      | 2.745            | 0.007         |
|       | 0.029      | 2.755            | 0.017         |
|       | 0.043      | 2.760            | 0.022         |
|       | 0.065      | 2.777            | 0.039         |

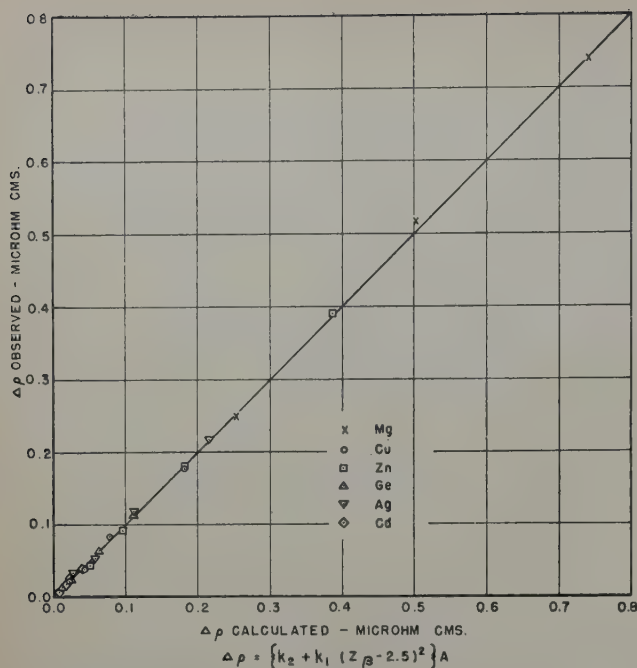


Fig. 7—Agreement between calculated and observed resistance of various solid solution alloys of aluminum.

to be insignificant. The sensitivity of the Kelvin bridge in the range which was used was slightly better than  $\pm 0.5$  pct. Total errors from these sources may have amounted to about  $\pm 0.5$  pct (or  $\pm 0.015$  microhm cm) of the calculated resistivity.

All resistance measurements were made at atmospheric temperature ( $22^\circ$  to  $26^\circ\text{C}$ ) and were corrected to  $24^\circ\text{C}$ . Since the temperature coefficient of resistivity of dilute alloys is known to be practically independent of composition,<sup>14</sup> a correction of 0.00429 microhm cm per  $^\circ\text{C}$  appropriate for 99.996 pct Al<sup>15</sup> was applied to each of the alloys.

### Experimental Results

The resistivities of the various alloys as a function of atomic percentage of the alloying element are given in Table III and plotted in Fig. 6. The usual linear increase of the resistivity of dilute solutions with atomic percentage of alloying element was obtained. The value for the electrical resistivity for pure aluminum was obtained by extrapolation of the data for each alloy series to zero concentration.

### Discussion and Conclusions

The atomic number and  $Z_\beta$  of each of the alloying elements used in this investigation are given in Table IV. Since elements Cu (29), Zn (30), and Ge (32) are in the same period of the periodic table, Norbury's rule as given by eq 1 was applied to the data

Table IV. Equation Constants Used for the Calculated Change in Resistance of the Aluminum Alloys

| Element | Atomic No. | $Z_\beta$ | $k_1$  | $k_2$  |
|---------|------------|-----------|--------|--------|
| Mg      | 12         | 2         | 1.832  | 0      |
| Al      | 13         | (2.5)     |        |        |
| Cu      | 29         | 1         | 0.2675 | 0.1731 |
| Zn      | 30         | 2         |        |        |
| Ge      | 32         | 4         |        |        |
| Ag      | 47         | 1         |        |        |
| Cd      | 48         | 2         | 0.2535 | 0.5446 |

obtained from these elements to determine  $k_1$ ,  $k_2$ , and  $Z_\alpha$ . The value of  $Z_\alpha$  thus obtained was 2.50 and indicates again that the aluminum ion in the metallic state has a charge of about  $-2.5$  electrons.

Using the values of  $k_1$  and  $k_2$  given in Table IV and assuming that the ionic charge of aluminum is  $-2.50$  electrons, the correlation between  $\Delta\rho$  calculated and  $\Delta\rho$  observed shown in Fig. 7 was obtained.

Thus, the effect of alloying additions of Cu, Zn, Ge, Ag, Cd, and Mg to aluminum on its electrical resistivity has been determined; and applying the Norbury rule to the resistivity of aluminum alloys suggests that the apparent valence of aluminum is approximately 2.5.

### Acknowledgments

This investigation was conducted under the sponsorship of the Office of Naval Research. The authors wish to express their appreciation to the O.N.R. for its continued interest throughout the course of these studies. They also wish to thank T. E. Tietz and A. Goldberg for their interest and criticism during the experimental phase, and Mrs. G. Pelatowski for her careful preparation of the figures. They are also very grateful to M. Nathans for his advice and suggestions which greatly facilitated this investigation.

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# Growth of Molybdenum Single Crystals

by N. K. Chen, R. Maddin, and R. B. Pond

A METHOD has been described by Andrade<sup>1</sup> for obtaining very rapid grain growth so that single crystals of high melting point metals could be made with comparative ease. The furnace construction was essentially a very thin wire through which was passed an electrical current so that "a high uniform temperature" was maintained. The wire was surrounded by a fused quartz tube from which the air had been evacuated. Andrade applied this method to the growth of single-crystal wires of alpha iron, and Tsien and Chow<sup>2</sup> prepared single crystals of molybdenum 0.25 mm diam in this way.

In the present report a method is described in which the basic idea of the Andrade furnace is utilized. However, modifications are employed so that large single crystals of molybdenum or of any refractory metals can be grown.

## Furnace

The modified Andrade furnace is shown in Fig. 1, and the detailed drawing of its construction can be seen in Fig. 2. The furnace proper consists of a 2½-in. diam fused silica tube, 20 in. long, which is evacuated continuously at the bottom. Two water-cooled copper electrodes hold the specimen by means of collets held in place in the electrodes by set screws. These electrodes serve also to transmit power to the specimen. The lower electrodes can be clamped to the stand, while the upper electrode is fastened in place to the bellows which in turn is further connected to one side of the lever arm, flexibly supported at the top. After the specimen is mounted and the vacuum is secured, the lever arm is adjusted by means of the counter weight so

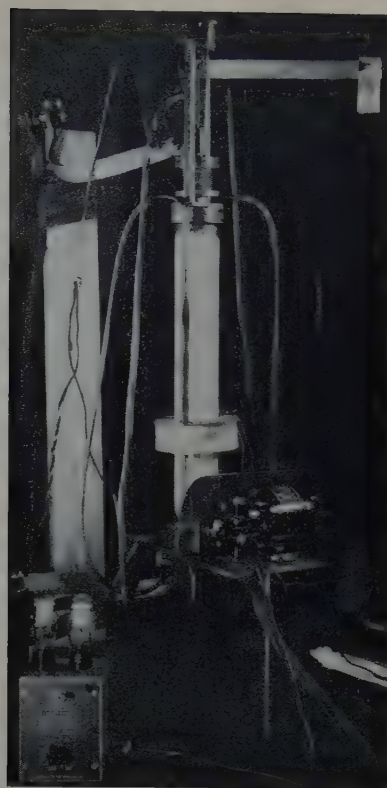


Fig. 1—Modified Andrade furnace.

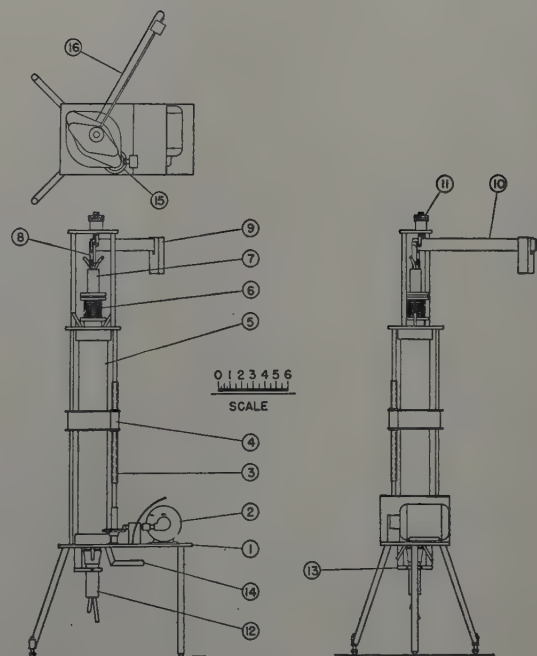


Fig. 2—Details of modified Andrade furnace.

- |                                                 |                         |
|-------------------------------------------------|-------------------------|
| 1—Motor and tube support                        | 8—Flexible link         |
| 2—Electric motor for raising subsidiary furnace | 9—Beam weight           |
| 3—Jack screw                                    | 10—Beam                 |
| 4—Subsidiary furnace (nichrome)                 | 11—Adjusting screw      |
| 5—Fused silica tube                             | 12—Lower electrode      |
| 6—Bellows                                       | 13—Lower electrode lock |
| 7—Upper electrode                               | 14—Gas outlet           |
|                                                 | 15—Reduction gears      |
|                                                 | 16—Indicating needle    |

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that the bellows is at its relaxed position. This insures that the total weight of the specimen, the upper electrode, and the downpull of the vacuum are balanced by the horizontal beam. Any expansion of the specimen on heating should proceed freely, if other frictional forces could be neglected. During the time of heating the specimen, the beam is maintained in a horizontal position by turning the nut at the top, the rotation of the electrode is prevented by a key fitted into a groove. This arrangement proved very desirable in that buckling of the specimen during the high temperature treatment was avoided.

The power is supplied by a motor generator set with a capacity of 550 amp at a maximum of 24 v. Results indicated that for a  $\frac{1}{8}$ -in. diam, 6-in. long molybdenum rod, a current in the vicinity of 210 amp at 2.5 v could heat the specimen up to an average temperature of 2000°C.

The subsidiary external furnace is wound with nichrome so that the electric heating zone is a cylindrical band  $\frac{1}{2}$  in. wide. It can be raised or lowered by the attached motor whose speed may be varied by means of an electronic controller from 0.5 to 15 in. per hr.

### Temperature Measurement

The average temperature of the specimen can be measured from the change in its resistance with temperature. As may be seen in Fig. 3, a linear relationship of specific resistance of molybdenum with temperature exists up to its melting point.<sup>8</sup> Thus, when the total current is measured, together with the voltage drop across the specimen, the corresponding resistance can be used to indicate the average temperature. Fig. 4 shows the E-I characteristic curve, measured for three specimens of  $\frac{1}{8}$ -in. Fansteel molybdenum rod, 6 in. long. The current through the specimen is adjusted by controlling the field resistance of the generator with electric stoves and a rheostat. After the current and voltage have been stabilized corresponding to a particular average temperature of the specimen, this equilibrium condition can be maintained for a long time.

### Experimental Results

The original material used was  $\frac{1}{8}$  and  $\frac{1}{4}$ -in. diam, 6-in. long Fansteel molybdenum with a grain size far smaller than could be denoted by any ASTM designation, as shown in Fig. 5. Its longitudinal section exhibited long fibrous grains, Fig. 6. The first specimen, M-1, was heated to an average temperature of about 2000°C for 90 min. Since no arrangement was designed to account for the ex-

pansion of the specimen in this first run, the specimen buckled and broke into three pieces, with a brittle fracture, when disassembled from the furnace. Nevertheless, back-reflection Laue photographs exhibited a large amount of grain growth in this short period of heat treatment, as shown in Fig. 7. Three other specimens, M-2, M-3, and M-4, were heated in the furnace according to the time-temperature curve shown in Fig. 8. These attempts still resulted in buckling of the specimens which was probably due to the force necessary to overcome friction in the system, namely, friction of the electrodes against the surface of their receptacles. This was overcome by minimizing the friction.

From Fig. 7 it may be concluded that all three specimens resulted in single crystals of certain lengths. M-3 revealed three grains thermally etched, each extending through the whole crystal with lengths of  $\frac{3}{4}$  to  $1\frac{1}{4}$  in. The surface of the specimen was bright, the grain boundaries being clearly revealed when the specimen was removed from the furnace. All specimens were electrolytically polished using an electrolyte of 300 cc methyl alcohol, 60 cc  $H_2SO_4$ , 130 cc HCl, and a current density of 4 amp per sq in. After etching with NaOH-KFe<sub>3</sub>(CN)<sub>6</sub> solution, the grain boundaries of the large grains, as well as some surface grains distributed as islands in the large grains, could be observed. Thus M-2 showed a grain about  $\frac{2}{5}$  in. in length which confirmed the X-ray observations shown in Fig. 7, although the lower middle photographs, M-2, exhibited three grains and M-4 two large grains about  $1\frac{1}{4}$  in. long extending through the whole specimen. The polycrystalline material shown adjacent to the large single grain in Fig. 9 had an average ASTM grain size of No. 3. With the  $\frac{1}{4}$ -in. material it was found necessary to recrystallize the as-received molybdenum rod and to extend the specimen 1 to 2 pct in order to provide a strain. Following this procedure, a total of 7 hr was required to produce single crystals approximately  $1\frac{1}{2}$  in. long.

While the specimen was maintained at high temperature, considerable evaporation occurred and a film of metal formed on the inside wall of the silica tube. The zone of this deposition extended through the middle 6 in. of the tube.

### Discussion

The modified Andrade equipment has overcome the limitations of the original Andrade method in

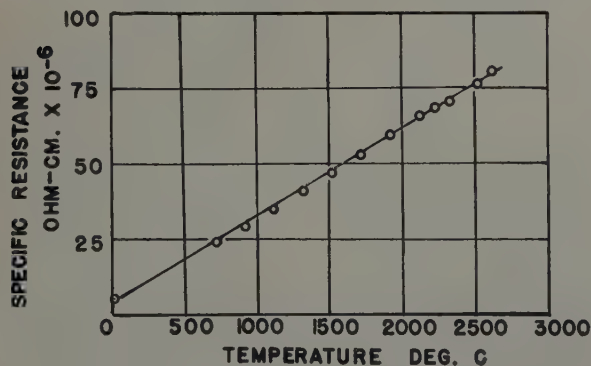


Fig. 3—Effect of temperature on electrical resistance of molybdenum.

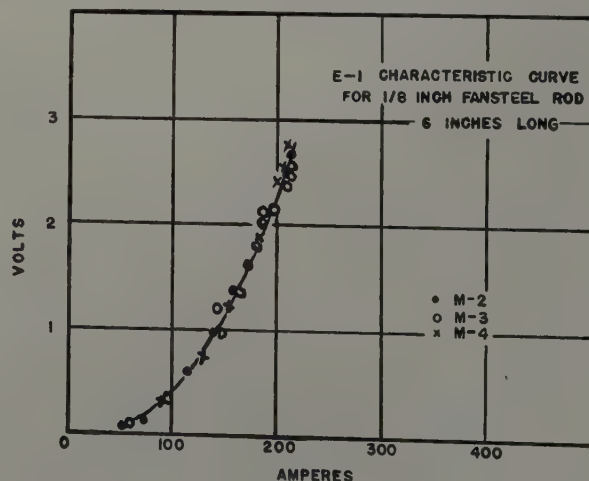
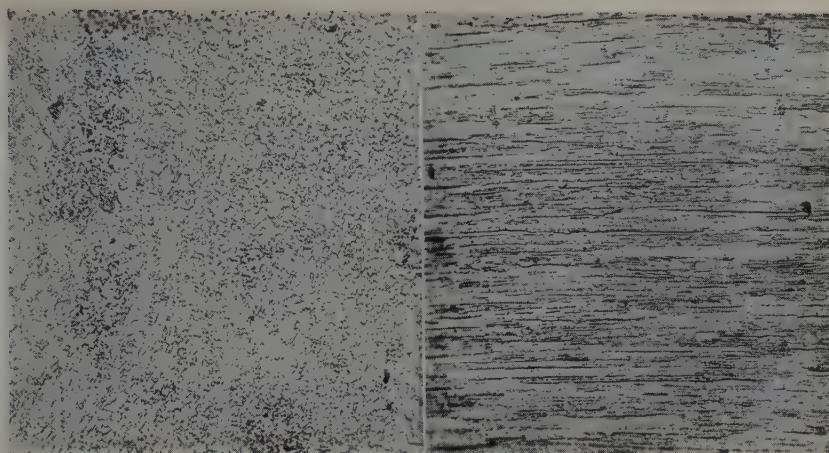


Fig. 4—E-I characteristic curve for  $\frac{1}{8}$ -in. Fansteel molybdenum rod 6 in. long.



Fig. 5 (left)—Grain size of as-received Fansteel molybdenum  $\frac{1}{8}$ -in. rod cross-section. Etchant  $\text{NaOH}:\text{K}_3\text{Fe}(\text{CN})_6$ . X100.

Fig. 6 (right)—Grain size of as-received Fansteel molybdenum  $\frac{1}{8}$ -in. rod longitudinal section. Etchant  $\text{NaOH}:\text{K}_3\text{Fe}(\text{CN})_6$ . X100.



that only very fine wire could be used with his equipment as a starting material. With the present arrangement, material of rather large size, i.e.,  $\frac{1}{2}$ -in. rod, can be converted into single crystalline form.

The very rapid grain growth observed in these experiments over the relatively short time employed is of great interest. Since both ends of the specimen are at room temperature, about  $35^\circ\text{C}$ , where the center section is maintained at a temperature higher than  $2000^\circ\text{C}$ , a very sharp temperature gradient exists in the specimen. It is not known whether the sharp gradient or the high temperature is responsible for the rapid grain growth, nor is it possible at the present time and with the present equipment to measure or calculate accurately the temperature gradient along the rod. A simple uniform variation of temperature was assumed and the average temperature resulting

from this distribution was calculated. With this assumed temperature gradient the total average resistance assuming different lengths of rod was determined. By this method the temperature of the rod was calculated as shown in Fig. 8. There was little doubt that the temperature at the center of the rod exceeded  $2000^\circ\text{C}$  when the average temperature for a length of 4 in. was measured as  $2000^\circ\text{C}$ .

It is interesting to note that Tsien and Chow, in their original experiments, used the subsidiary furnace "to establish a temperature gradient." Without the use of the subsidiary furnace, single crystals never exceeded 2 mm in length. However, it is probable that the external furnace has little or no effect on the final outcome of the experiments since the sharpest temperature gradient exists in the specimen itself as a result of the water-cooled ends.

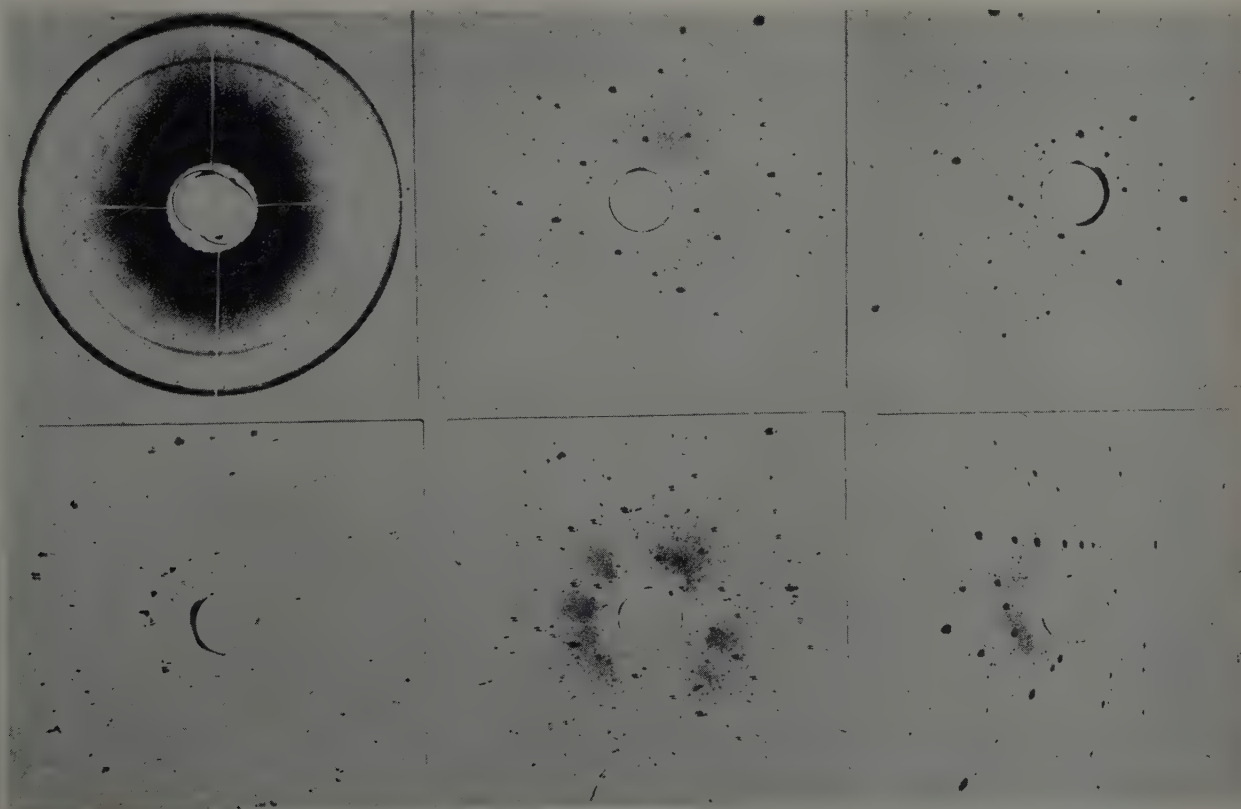


Fig. 7—Back-reflection Laue photographs. Specimens M-2, M-3, and M-4 were treated as shown in Fig. 8. Original material, upper left. Specimen M-1, 40 min at  $2000^\circ\text{C}$ , lower left. Specimen M-2, upper center. Specimen M-2, lower center. Specimen M-3, upper right. Specimen M-4, lower right.

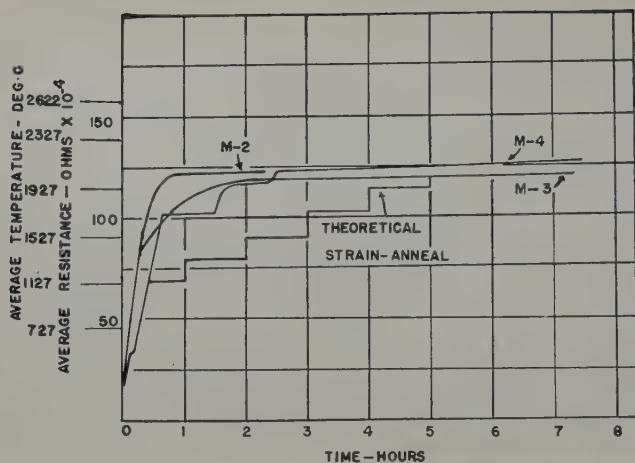
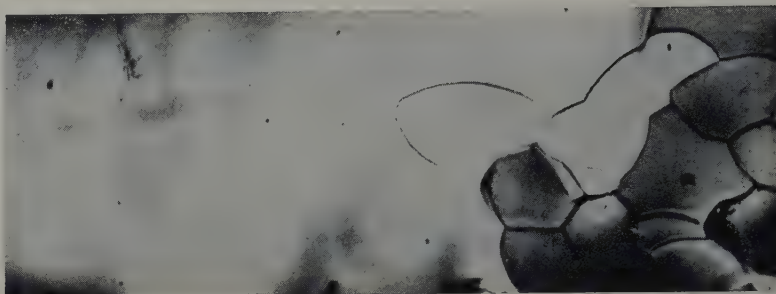


Fig. 8 (left)—Time-temperature curve showing heating process of specimens M-2, M-3, and M-4.

Fig. 9 (right)—Interface between single crystal and fine grained molybdenum rod. Electrolytically polished. Etchant,  $\text{NaOH}:\text{K}_3\text{Fe}(\text{CN})_6$ . X150.



No observable difference in the results could be noted when the external furnace was used in the present case.

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of the furnace and L. G. Richards for metallographic work is gratefully acknowledged.

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- <sup>3</sup>*Molybdenum Steels, Irons, Alloys*. p. 362 (1948) New York. Climax Molybdenum Co.

#### Corrections

In the February 1951 issue: *Observations on Rimming Steel Ingots* by A. Hultgren, G. Phragmen, S. Wohlfahrt and J. E. Ostberg. P. 103, in the footnote  $\gamma$  transformation should read  $\delta$  to  $\gamma$  transformation. P. 105, the last sentence of the ninth paragraph, col. 1, should read: "In the middle portion along the axis, a set of fine pores is seen." In the next paragraph, the next to the last sentence should read: "For this reason the final stage of freezing was associated with a small amount of shrinkage and, in consequence, only small pores and few blowholes were formed." P. 110, in the last sentence H. Gillo should read H. Gille.

In the February 1951 issue: TP 3002E. *Effect of Ternary Additions on the Age-Hardening of a Copper-Silver Alloy* by Harold Margolin and Walter R. Hibbard, Jr. P. 176, Table II, under the heading "3rd Element, Wt Pct" the value for Cu-Ag-Zn should be 0.975 and not 0.075.

In the December 1949 issue: *The Properties of Sand Cast Magnesium-Rare Earth Alloys* by Thomas E. Leontis. P. 974, in Table VII, the tabulated creep limits for 300°F are actually the values for 400°F, which are the same as those plotted in Figs. 18, 19, and 20. The values intended for Table VII under 300°F are as follows:

| Table VII. Creep Limits at 500°F |                  |                               |                               |                               |  |
|----------------------------------|------------------|-------------------------------|-------------------------------|-------------------------------|--|
| Alloy No.                        | Composition, Pct | Creep Limit, 1000 psi         |                               |                               |  |
|                                  |                  | 0.1 Pct<br>Creep<br>Extension | 0.2 Pct<br>Total<br>Extension | 0.5 Pct<br>Total<br>Extension |  |
| 300°F                            |                  |                               |                               |                               |  |
| 2                                | 0.40 Mischmetal  | 7.8                           | 6.2                           | 8.0                           |  |
| 3                                | 1.15 Mischmetal  | 7.9                           | 6.1                           | 7.2                           |  |
| 5                                | 1.62 Mischmetal  | 8.5                           | 6.4                           | 8.3                           |  |
| 6                                | 2.50 Mischmetal  | 9.7                           | 7.3                           | 9.2                           |  |
| 7                                | 2.85 Mischmetal  | 12.2                          | 9.0                           | 11.0                          |  |
| 8                                | 3.23 Mischmetal  | 13.0                          | 10.0                          | 12.3                          |  |
| 9                                | 6.33 Mischmetal  | 15.5                          | 12.0                          | 14.8                          |  |



# Relationships Between Germanium and Cadmium In the Electrolysis of Zinc Sulphate Solutions

by S. T. Ross and J. L. Bray

The paper provides electrometallurgical data on the problem of germanium removal from zinc sulphate solutions. Germanium traces have caused much concern to the zinc refiner. Confirmatory evidence of interaction between germanium and cadmium is presented. Statistical analysis of data expands its significance and enhances its value. Further research is outlined.

THE literature contains many references to the effects of trace amounts of germanium in the production of electrolytic zinc. One of the authors had experience with this troublesome element as early as 1917 at Trail, B. C. In 1929, Tainton and Clayton<sup>1</sup> reported that concentrations of as little as one part per million of germanium were sufficient to cause serious losses in current efficiency. Liddell<sup>2</sup> reported that trace amounts of germanium cause marked lowering of the hydrogen overvoltage of electrolytic zinc cells, so that commercial production was impaired. Bray<sup>3</sup> recorded the history of germanium in relation to electrolytic zinc production, noting that concentrations below 10 ppm have been found to yield low current efficiencies and copious hydrogen evolution. Koehler<sup>4</sup> stated that germanium "when present to the extent of a small fraction of one part per million per liter, causes serious evolution of hydrogen with a corresponding reduction in current efficiency."

Recently, however, S. W. Ross<sup>5</sup> reported, from Risdon, Tasmania, that "in the course of leaching ... dissolved traces of germanium ... if not removed almost completely ... increase the reversion of cadmium during the filtration of the copper-cadmium precipitate and reduce the current efficiency during subsequent analysis." The copper-cadmium precipitate referred to is the residue from the zinc-dusting purification of zinc sulphate leach solutions.

In the face of such conflicting testimony and with the increasing industrial importance of pure germanium and zinc it was decided to investigate the relationship between cadmium and germanium. Furthermore, other work by the authors showed certain discrepancies to exist in the theories of Tainton, et al. In the laboratory, without marked efficiency decreases, the authors have deposited zinc successfully from solutions containing as high as 1 g per liter of germanium. This could be done only when there was no cadmium present.

Preliminary investigations of the suspected rela-

tionships were carried out by means of emission spectrographic analysis using a beryllium internal standard. Several solutions containing 100 g per liter of zinc, as zinc sulphate, and 1 g per liter of cadmium, as cadmium chloride, were prepared. These concentrations were on the order of those obtained during a commercial low-acid leaching process. Varying concentrations of germanium were added to these solutions so that the range of 0.0000 to 0.5000 g per liter of germanium was covered. A 250 ml sample of each solution was agitated with 2.5 g of zinc dust for 30 min, filtered, and the filtrates were examined spectroscopically. Qualitative evidences of cadmium traces were found in those filtrates which originally contained above 10 ppm of germanium. Reliability of the analytical method did not permit quantitative investigations since cad-

Table I. Current Efficiencies Obtained at 0.0000 and 1.5000 G per Liter Cadmium Concentrations

| Ge Concentration,*<br>G per Liter | Cd Concentration,*<br>G per Liter | Efficiency,<br>Pct |
|-----------------------------------|-----------------------------------|--------------------|
| 0.0000                            | 0.0000                            | 94.270             |
| 0.0010                            | 0.0000                            | 94.849             |
| 0.0050                            | 0.0000                            | 92.649             |
| 0.0075                            | 0.0000                            | 94.039             |
| 0.0100                            | 0.0000                            | 96.084             |
| 0.0000                            | 1.5000                            | 93.460             |
| 0.0010                            | 1.5000                            | 95.158             |
| 0.0050                            | 1.5000                            | 92.148             |
| 0.0075                            | 1.5000                            | 91.260             |
| 0.0100                            | 1.5000                            | 84.546             |

\* Cd and Ge concentrations shown are those existing before zinc-dust purification.

mium determination in the concentrations present in zinc-dusted solutions lacks sufficient sensitivity for reproducible results.

As a consequence of the inability of the investigators to obtain acceptable results through direct quantitative analysis, an indirect approach was devised. This indirect method involved a study of the current efficiency, in a model zinc cell, as a function of the concentrations of cadmium and germanium. Variables such as cell temperature, voltage, current density, anode spacing, relative electrode area, degree of agitation, cathode preparation technique, time, acid concentration, and solution volume were held constant.

Fig. 1 shows the cell used. The current was fur-

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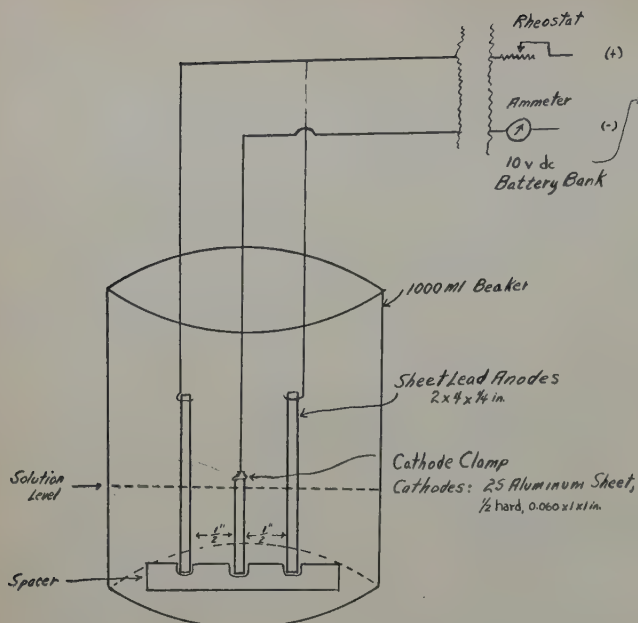


Fig. 1—Model zinc cell.

nished by a 10 v storage battery bank. The anodes were high purity sheet lead, approximately 2x4x $\frac{1}{4}$  in. The cathodes of 2S aluminum alloy sheets were 0.060 in. thick,  $\frac{1}{2}$  hard, cut into 1-in. squares. The anodes were separated by a wooden spacer which had been dipped in paraffin to prevent possible side reactions from occurring. The current was kept constant at 0.425 amp for each run—a current density of approximately 30 amp per sq ft. Each run was accomplished at room temperature without agitation. Each solution contained 100 g of zinc per liter, as zinc sulphate, and each run was made with a 250 ml volume of solution. Each cathode was degreased with trichloroethylene before electrolysis. Each solution was treated with 2.5 g of zinc dust for 30 min, with agitation, and filtered before electrolysis. Measurements were taken of the weight of each

cathode before and after electrodeposition, and the weight of zinc deposited was obtained as a difference. The current efficiency of each run was calculated according to Faraday's law.

### Experimental Results

Table I lists the analyses, before zinc dusting, and current efficiencies obtained from solutions varying from 0.0000 to 0.0100 g per liter of germanium at the 0.0000 and 1.5000 g per liter concentration levels of cadmium. The time of each run was 30 min. Fig. 2 shows that the current efficiency, when plotted against the germanium concentration, tends to drop off rather sharply with increasing germanium content at the 1.5000 g per liter level of cadmium concentration, while remaining relatively constant at the 0.0000 g per liter cadmium concentration level.

**Expanded Data:** For evidence of the interaction between cadmium and germanium, the data were expanded and an analysis of variance was performed. For cadmium concentrations of 0.0000 to 2.5000 g per liter in combination with germanium contents of 0.0000 to 0.1000 g per liter, three plating runs were made for each zinc sulphate solution. The runs were of 60, 30, and 15 min duration to obtain replication of the statistics, as well as to investigate the variable of plating time. All other factors were

Table II. Effect of Germanium and Cadmium on Current Efficiency\*

| Cd,<br>G per<br>Liter | Time,<br>Min. | Ge, G per Liter |        |        |        |        |
|-----------------------|---------------|-----------------|--------|--------|--------|--------|
|                       |               | 0.0000          | 0.0010 | 0.0050 | 0.0075 | 0.0100 |
| 0.0000                | 60            | 96.971          | 94.540 | 94.270 | 90.122 | 95.273 |
|                       | 30            | 94.270          | 94.849 | 92.649 | 94.039 | 96.084 |
|                       | 15            | 92.997          | 94.077 | 96.238 | 89.524 | 92.379 |
| 1.0000                | 60            | 96.991          | 94.347 | 94.223 | 92.186 | 87.402 |
|                       | 30            | 95.505          | 93.730 | 88.521 | 91.878 | 82.269 |
|                       | 15            | 94.694          | 92.071 | 90.373 | 89.292 | 88.058 |
| 1.5000                | 60            | 95.119          | 94.521 | 93.317 | 92.206 | 84.321 |
|                       | 30            | 93.460          | 95.158 | 92.148 | 91.260 | 84.546 |
|                       | 15            | 95.003          | 94.154 | 88.058 | 90.681 | 84.893 |
| 2.0000                | 60            | 92.997          | 94.965 | 92.977 | 84.276 | 88.135 |
|                       | 30            | 94.965          | 93.614 | 91.341 | 89.833 | 82.688 |
|                       | 15            | 93.769          | 94.077 | 90.604 | 86.051 | 83.712 |
| 2.5000                | 60            | 95.659          | 95.158 | 92.611 | 88.289 | 87.446 |
|                       | 30            | 94.077          | 95.505 | 91.120 | 89.138 | 83.418 |
|                       | 15            | 94.926          | 94.617 | 87.980 | 87.517 | 85.125 |

\* These statistics were obtained from conversion of the weights of deposited zinc through the application of Faraday's law. The statistics are current efficiencies in percent. Percent current efficiencies =  $\text{Wt Zn} \times 1157.636 \div \text{Cadmium and germanium concentrations shown are those existing before zinc-dust purification.}$

Time in min

held constant, as described before. Table II shows the tabulated results of 75 runs made in random order. Randomization was achieved by assigning numbers 1 to 75 to each run, and performing each run in the order in which its number appeared in a table of random numbers as prepared by Fisher and Yates.<sup>6</sup> Randomness was desired to remove as much of the cumulative effects of error as possible (e.g., possible effects due to a build-up of anode reaction products in the solutions, etc.).

**Analysis of Variance:** An analysis of variance was performed on the data of Table II using the method of Freeman.<sup>7</sup> Essentially, the method consisted of obtaining the variance due to each factor, or combination of factors, and comparing it for significance with the variance due to error.

The significance of the interaction of cadmium and germanium concentrations was thus established. By indirect means, it substantiated the fact, only

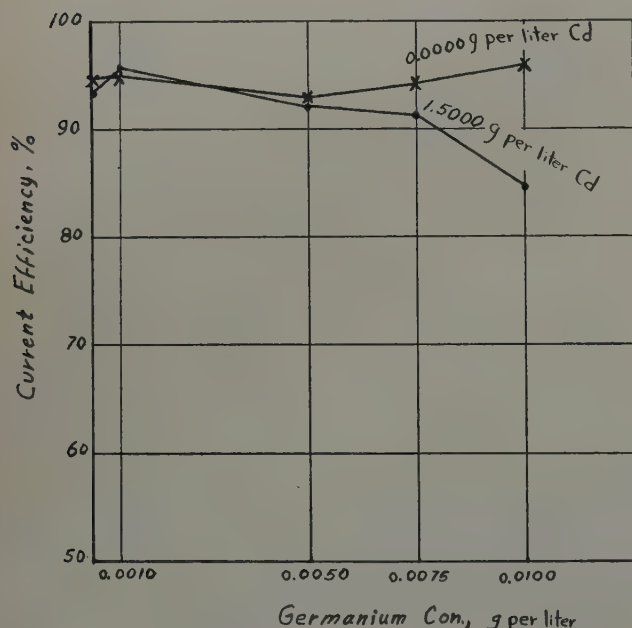


Fig. 2—Current efficiencies at 0.0000 and 1.5000 g per liter Cd levels.



hinted at by the spectrograph, that the chemical interaction of germanium and cadmium is of significance in consideration of electrolytic zinc cell problems. Analysis of variance showed that the interaction of germanium and cadmium was of such statistical importance that it must be regarded as a factor in the variation of cell current efficiencies due to other than random causes.

**Significance of Difference:** To obtain further evidence of the relationship between germanium and cadmium, the solutions on the 0.0000 and the 1.0000 g per liter levels of cadmium concentrations were investigated in a somewhat different manner. A test for the significance of the difference of the means of these two groups of data was made. The methods of "Student"<sup>8</sup> and Fisher<sup>9</sup> were followed.

Such calculations indicated that a statistically significant difference existed between mean values of the data. The primary assignable cause of that difference was variation of the cadmium concentration. Such random errors as may have been introduced by slight fluctuations of other variables were minimized by the method of calculation.

### Summary and Conclusions

The significance of difference and analysis of variance tests as performed on the above data substantiate the claim that definite interaction exists in the zinc cell between cadmium and germanium concentrations. Germanium alone, within normal operating limits, does not cause large current efficiency losses. Rather, this research indicates that the adverse effects of germanium are notably enhanced by the presence of cadmium, and that the presence of germanium in leach solutions of the commercial zinc sulphate type precludes the complete removal of cadmium from them. This leads to further ques-

tions, as yet unsettled. What, if any, are the effects of the interactions of other impurities such as arsenic, antimony, bismuth, and lead, in the minute quantities found present after purification by present methods? How is the cell overvoltage affected by these interactions? What is the physical-chemical answer to the existence of such interactions? These are now being investigated in this laboratory.

While the answers to these questions are of academic interest, the commercial picture remains the same. Regardless of the nature of the interactions, germanium and cadmium must be removed in sufficient quantity before efficient electrowinning of germanium-tainted ores can be accomplished. It does not matter to the zinc producer whether germanium causes efficiency losses directly, or whether germanium and cadmium cause efficiency losses. In either event, the difficulty is there and a remedy must be found.

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- <sup>5</sup> S. W. Ross: *Trans. AIME* (1949) **185**, p. 205; *JOURNAL OF METALS* (March 1949).
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### Technical Note

## Deformation Texture of Cold-Drawn Copper Wire

by Walter R. Hibbard, Jr.

BACKOFEN<sup>1</sup> reported recently that "the deformation texture of cold-drawn OFHC copper wire, after a reduction in area of 97.3 pct, may still be described as a composite of [111] and [100] directions aligned parallel to the wire axis." In the introduction, he indicated that this was in contrast to the work of Hibbard,<sup>2</sup> who reported a single [111] texture after a reduction of 96.4 pct. Unfortunately Backofen stated that this was a reduction in area when actually it was a reduction in diameter, as is clearly stated in the reference. Moreover, the results of Backofen are in complete agreement with the results of Hibbard. Backofen's 97.3 pct reduction in area is an 83.3 pct reduction in diameter, after which he found a double [111] and [100] texture with the former predominating. Similarly, Hibbard,<sup>2</sup> after an 86 pct reduction in diameter found a double [111] and [100] texture with the former predom-

inating. Hibbard, however, when he drew the wire further to 96.4 pct reduction in diameter, found primarily a single [111] texture as illustrated by Fig. 2 of ref. 3. Here also, Hibbard<sup>3</sup> reported evidences of the [100] recrystallization texture found by Backofen. It might also be pointed out that Backofen not only drew his wire 97.3 pct reduction in area but also etched them over 99 pct reduction in area from 0.125 to 0.01 in. diam. Hibbard's wires were drawn directly to size.

In summary, the deformation texture of cold-drawn copper wire still may be described as primarily a single [111] texture after a sufficient amount of drawing, such as 96.4 pct reduction in diameter.<sup>2,3</sup>

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- <sup>1</sup> W. A. Backofen: *JOURNAL OF METALS* (March 1951), *Trans. AIME*, p. 250.
- <sup>2</sup> W. R. Hibbard, Jr.: *Trans. AIME* (1949) **185**, p. 598; *JOURNAL OF METALS* (Sept. 1949).
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TN 75E. Manuscript, March 12, 1951.

# Electric Furnace Melting Of Copper at Baltimore

by Peter R. Drummond

THE final casting of refined copper has been restricted for generations by the following sequence of operations: Filling the reverberatory furnace, melting, skimming, blowing or flapping, and poling. The hoped-for 24 hr cycle, producing 300 tons or more, has been taken up largely with the necessary but time-consuming tasks of cleaning the bath, sulphur elimination, and in turn removal of excess oxygen to produce tough-pitch copper. Incidental to comparatively slow melting under combustion gases, copper oxides react with the furnace lining, and the slag so-formed must be completely recycled.

The three-phase arc furnace has eliminated some of the cycle stages, and telescoped the remainder into a continuous operation. Electrical energy, supplied to graphite electrodes enclosed in high grade refractories, rapidly melts copper cathodes and sustains a stream of metal, containing approximately 0.01 pct oxygen, without contamination from fuel.

The arc was struck on the first large electric furnace for melting copper in the United States on April 13, 1949. The earliest use of this type of furnace was at Copper Cliff, Ont., in 1936, and an admirable description of their installation has been published.<sup>1</sup> Copper, melted in the Baltimore furnace, is used to cast billets, and the installation differs somewhat from the Canadian, as will be described.

The arc furnace is a heavy-duty, three-phase furnace, holding 50 tons, the general outline of which appears on Fig. 1. The steel shell is 15 ft ID with a bottom radius of 14 ft 2 in. The roof, separate and distinct from the body, consists of a 15-ft water-cooled, cast-steel ring of the same outside diameter as the furnace. The center line of the furnace lies 9 ft 6 in. from that of the trunnions, permitting a 5° backward tilt for skimming, and a 40° maximum nose tilt forward for complete draining. Normally, the furnace overflows by displacement, and the use of the forward tilt arrangement is restricted to covering charging delays.

The charging slot, 3 ft 8 in. x 5 in., lies on the north center line, the tap hole on the south, and the 30x30 in. skim door 45° to the west of the slot.

The original 20-in. graphite electrodes were replaced with 14 in. in December 1949. Three conventional direct current winch drives, governed by electrical controls, position each electrode which has individual mast supports and counterweights. An independent circulation supplies cooling water for the

electrode glands, the roof ring, charge slot, and the skim door frame.

## Arc Furnace Refractories

**Hearth:** Fused-in monolithic bottoms had been used in copper arc furnaces, installed prior to April 1949. These consisted of thin layers of periclase, successively fused in place over preliminary brick courses. Heat was obtained from the arc, using a T-like arrangement of broken electrodes resting directly on the periclase to be fused. The operation, taking weeks to perform, was very expensive. The chemically-bonded magnesite-brick bottom, installed at Baltimore, was the first of its kind and a radical departure from previous practice.

It consists of a 1 to 6-in. layer of castable refractory laid on the steel shell, modifying it to a 12 ft 2 in. bottom radius. Two courses of 9x2½-in. fireclay straights and keys follow.

The third course is made of 9-in. magnesite blocks of special shape to form circles of an inverted arch. It was started by a four piece keystone with skewbacks forming the outer course. The fourth course also started on a central keystone, or button, of four 90° segments, 12 in. diam x 13½ in. deep, and continued with 13½-in. blocks. Skewbacks at the shell completed the course to produce a horizontal surface for the side walls with a single course of No. 2 arch fireclay against the steel.

Dry chrome-magnesite cement was brushed over each course after laying, and a 1-in. expansion space between the brick and the shell was filled with the same mixture. The total bottom thickness, excluding the castable material, was 5 in. of clay plus 22½ in. of chemically-bonded magnesite.

**Tap Hole:** A 5-in. OD and 3-in. ID silicon-carbide tube constitutes the tap hole and is set tangential to the upper course of the furnace bottom. Molten metal fills the tube when the furnace is level and filled to capacity.

**Side Walls:** The lining, against the shell, consists of a 9x4½x3 in. soldier course of fireclay, using straights and No. 1 arches to turn the circles. A second soldier course of 9x4½x2½-in. fireclay was laid in a somewhat similar fashion.

Three courses of 13½x6x3 in. and 9x6x3 in. of final magnesite, laid flat, completed the lining, using Nos. 1 and 2 keys to turn the circles. Cardboard spacers were placed between every two bricks in horizontal courses, and a thin coat of chrome-magnesite cement filled the joints between the firebrick and magnesite. A sprung-arch spanned the skim door with jambs of suitable magnesite shapes.

**Charge Slot:** The slot is 3 ft 8 in. wide x 5 in. high. A silicon-carbide sill of special shapes has a 30° slope to allow cathodes to slide easily into the bath. The original arch was flat, and composed of Nos. 1 and 2 wedge magnesite with a 6-ft radius. It projected 5 in. over the sill, and, being a flat arch, gave an 18 15/16-in. opening between the inner edge and the metal line. The whole assembly was later raised 9 in., and the flat arch replaced with an arch, the lower edge of which maintained the 5-in. width from the outer to inner edges as shown in Fig. 2. A water-cooled, cast-copper jacket protects the steel shell behind the slot.

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<sup>1</sup> Trans. Canadian Inst. of Min. and Met. (1946) 49, pp 199-222.



**Roof:** A single course of fire-clay skewbacks of special shape encircle the water-cooled ring. The remainder of the roof embodies standard sprung-arch construction, using bonded 9-in. magnesite of 3 and 2½-in. arches, straights, and wedges with special shapes as required to turn the circles, and with cardboard expansion joints between every fifth brick. The three electrode openings and a vent are turned respectively with 13½x4½x2½ in. and 9x4½x2½ in. magnesite arches.

**Launder:** A 30-ft steel-framed launder, a cross-section of which appears on Fig. 1, connects the arc furnace with a low frequency induction furnace. Three 9x4½x2½-in. silica insulating brick line the bottom with a course along each side, laid flat, leaving 2-in. side spaces which are both filled with loose silica insulation. Suitable fireclay shapes support the central silicon-carbide V channel, formed with one 1½-in. split laid flat and two 9-in. splits at a 60° angle, giving a roughly equilateral channel 9 in. deep x 10 in. wide at the top. Joints are filled with silicon-carbide cement. Courses of clay brick, two of 12x12x2 in. and one of 12x6x3 in. cover the channel.

**Induction Furnace:** This holds about 5 tons, appears in outline on Fig. 3, and serves merely as a reservoir between the arc and the casting ladles. Power control will be described under electrical equipment. Metal enters the unit from the launder through a 6 in. OD x 4 in. ID silicon-carbide tube inserted through one furnace trunnion. The furnace pours into casting ladles through a similar tube set at an angle to allow complete drainage without going beyond 90° from the vertical.

The unit comprises two sections: A body and separate induction slot. A steel casing constitutes the vertical shell and is lined with one soldier course of 4½-in. insulating firebrick and a course of chemically bonded 9-in. magnesite keys. The steel roof cover is filled with a castable refractory and clamps to the shell. A rammed 9-in. Mullite bottom is connected with the slot proper through an opening 24½x6 in. tapering to 21½x3 in.

The induction unit bolts to the foregoing. Each unit is rammed with Mullite, containing 6 pct moisture. This requires considerable technique, and once started, is carried to completion in 10 to 12 hr without interruption. After ramming, the units are heated electrically and dried before being put into service.

Two thermocouples, lying against the metal core bushing of the primary induction unit, connect with a recording potentiometer, by means of which core failure can be predicted. An independent 750 psi hydraulic system is used to tilt the induction unit for pouring about one ton of metal in 34 sec.

**Charging Machine:** Cathodes, to be charged to the arc furnace, are piled 20 high on pallets and travel by gravity on rollers to a shear, where the loops are removed. The cathode is then pushed into the charging machine magazine, which constitutes a novel feature of the installation.

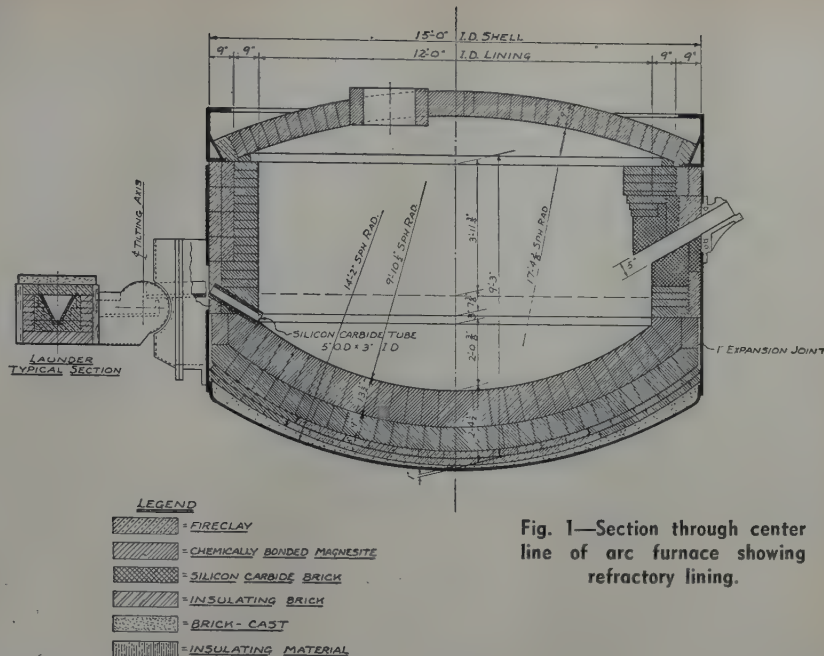


Fig. 1—Section through center line of arc furnace showing refractory lining.

The storage magazine consists of two endless parallel chain conveyors, mounted on a frame at 60° from the horizontal, to hold the cathodes. The chains carry a series of parallel plates, which form slots, and as a cathode comes to rest on one of them, its weight actuates a switch, energizing the drive motor to move the magazine one position upwards and so insure the presence of one sheet at a time in each slot. Fully loaded, the magazine holds approximately a 30-min supply for the furnace, and one man per shift can handle all charging into the furnace.

An elevating mechanism is interposed between the storage magazine and the furnace charging slot. This descends on tracks until two hooked members intercept the first closed pair of magazine gates, holding the topmost cathode. The members energize suitable relays, stop the elevator, open the gates allowing the cathode to slide into the elevator, and, by automatically reversing the drive, return the carriage to the charging position.

A timer, which can be set to charge cathodes at any desired rate, controls two more or less simultaneous actions. It opens the furnace door and at the same time actuates a pusher which thrusts the cathodes through the slot. The ram withdraws, the furnace door closes automatically, and the elevator drops to continue the cycle.

**Electrical Equipment:** The local electric utility company supplies power over a three-phase 60-cycle, 13.8 kv overhead line supported on wooden poles and pin insulators. The line terminates 100 ft from the furnace substation, where it changes to a three-conductor leaded cable laid underground in fiber ducts.

The two-story furnace substation is of fireproof construction in conformity with the local building code. The first floor contains a six-section, high-voltage, metal-clad oil circuit breaker switch gear, station control battery, a necessary charging motor generator set, a furnace-rotating regulator set, and one six-circuit three-phase 440 v free-standing, metal-clad air circuit breaker switch gear serving arc furnace equipment. The second floor carries: one 250 kva—13.8 kv primary to 480 v secondary self-cooled, oil-insulated, single-phase, 60-cycle transformer for the low frequency induction furnace; one 6000 kva—13.8 kv primary to 85 to 225 v secondary,



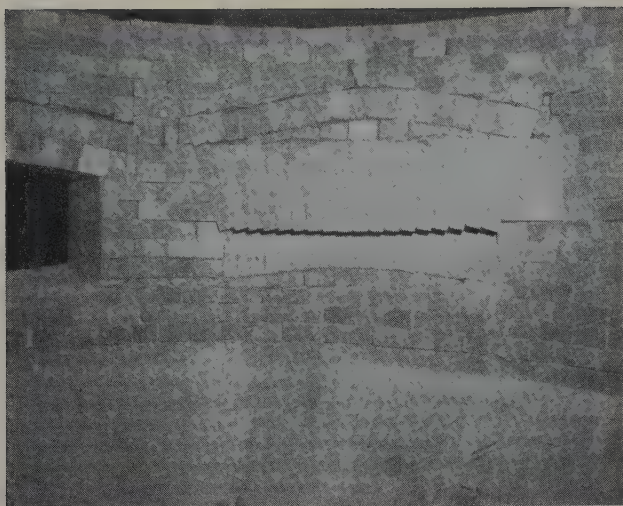


Fig. 2—Present charging slot.

water-cooled, oil-insulated, three-phase, 60-cycle transformer with tap changer for the arc furnace; and one 750 kva—13.8 kv primary to 480 v secondary, self-cooled, oil-insulated, three-phase, 60-cycle transformer serving arc furnace equipment.

The transformers stand directly above their respective oil circuit breakers and are wired with single conductor, varnished-cambric, flameproof cable through fiber ducts enclosed in steel. The floor is constructed to form a liquid-tight basin to take care of a possible transformer tank failure.

The arc furnace transformer is in line with the vertical center line of the furnace and at sufficient height to minimize the heavy rigid secondary copper buswork and to provide clearance and free movement for the flexible cable loops between the bus and the electrode mast arms. The bare copper cables, connecting the bus and mast arms, consist of twenty 1,500,000 circular mil and twelve 1,750,000 circular mil cables per phase.

The arc transformer secondary is connected in Y and the primary in delta. The primary taps permit the following secondary line to line volts: 225, 208, 190, 173, 156, 147, 130, 120, 110, 100, 90, and 85. At the present time the furnace is operated on 190, 173, 156, and 130 v.

The furnace operating control panel is flush with the station wall, and the back is readily accessible for inside repairs through a door adjacent to the panel. The main initiating control for the charging machine is on the same panel, in addition to conventional instrumentation and arc furnace controls.

A 12-lantern semaphore occupies a position to one side of the operating panel, and a solenoid-operated air whistle attracts the operator's attention to: 1—Tripping of any of the substation high voltage breakers, 2—power failure on the 250 v dc supply exciting either the rotating regulator or the electrode winch motor, 3—overheating of the arc furnace transformer, 4—low transformer oil levels, 5—power failure on the induction unit, 6—cooling fan failure, 7—high arc furnace side wall temperatures, 8—charging machine failure, and 9—failure of station control battery charging equipment.

A silicon-carbide target tube is set flush with inner side wall lining of the arc furnace, and a radiation pyrometer, sighted on this, indicates side wall temperatures which are recorded continuously. An adjustable contact-making device connects the recorder with the semaphore.

The low voltage, free-standing, metal-clad switch gear and controller for the induction furnace unit stands adjacent to the casting platform. This houses the main air circuit breaker, tapped autotransformer, power-factor correction capacitors, manual pre-setting tap switches, and magnetic solenoid tap changing contactor. Indicating power-factor and kilowatt meters, furnace molten metal electronic temperature recorder and controller, and furnace inductor core sleeve electronic temperature recorders are set flush on front of the switch gear cubicle.

The inductor core is rated 100 kva, the auto-transformer at 125 kva, 460 v, and is high tapped at 460, 440, and 380, with low at 250, 200, and 150. The manual selector switch preselects any one of both the high and low tap voltages. Then, the two solenoid-operated magnetic switches automatically control the furnace power input from the pre-selected taps. These, in turn, are dictated by electronic control received from the radiation pyrometer sighted on a silicon-carbide tube submerged in the metal bath.

The furnace currently operates on the 380 v high tap and 250 low, providing a power input of 65 and 30 kw respectively at 85 pct line power factor.

*Seasoning:* The brick hearth embodied a radical departure from previous practice, so, details of pre-heating and some history of the lining follow as contributory to the success of the furnace bottom.

Drying of the brick bottom began at 1:40 p. m., April 4, 1949, and the furnace was slowly brought to 2070°F by 7:20 a. m., April 11 by the use of an oil burner. The rise in temperature was controlled carefully by means of a thermocouple lying on the hearth with lead wires through the tap hole. The average rise was 11.8°F per hr.

After removing the burner, five tons of starting sheet scrap were charged. Six tons of ingots were then thrown on the cushion of scrap and the burner replaced. By 4 p. m. of the same day the charge was flat and the wall temperature 1900°F. The furnace was rocked back and forth intermittently until 11:10 p. m. to allow the molten metal to fill the interstices between the brick, the burner was then removed, and the furnace drained.

By 12:45 p. m. a second addition of 8.2 tons of starting sheets was charged. This was molten by 4:30 a. m., April 12, and ingots were then charged. By 9:15 a. m., 30.8 tons of ingots had been added. The charge was flat by 10:10 a. m., and the wall temperature 2020°F. Firing continued until 7:45 a. m. of the following day to raise the metal temperature. The burner was removed, and the electrodes lowered into the furnace. The side walls had reached 2120°F, and the arc was struck at 8:25 a. m. Power was used intermittently to familiarize the operators with the controls until 4:32 p. m. when cathode charging started.

The distinctive difference between burned-in bottom practice and the foregoing is that in burning in a bottom the arc is struck over a bare hearth whereas the brick bottom has never been subjected to direct radiation and possible local overheating. The wash-out charge made a copper-bonded monolith of the brick by allowing the metal to penetrate to a depth where it naturally froze, and the preliminary melt of 40 tons under oil assured that the bottom did not attain a temperature above that of the bath.

On Aug. 6, 1949, after 120 days of operation, the furnace was drained and cooled slowly, primarily



to replace the charging slot, the reason for which is explained below. Examination of the bottom at that time showed a slight build up of approximately  $\frac{1}{2}$  in. except for the central starting button of the upper course which had spalled to a depth of 2 in.

No repairs were made to the bottom, but a segment of the side wall, amounting to about one quarter of the circumference and including the skim door and charging slot, was replaced. A hot-metal charging slot was cut in the wall near the tap hole, and since then molten copper from the reverberatories has been used for the initial filling.

**Charging Slot:** The charging slot has been the cause of considerable delay. Copper accretions collect gradually in the opening, causing cathodes to jam. These accretions may be back splash from cathodes, metal surges caused by the arc, or a combination of both.

Details of the slot were presented in the general description, but it is noted again that the height of the opening increases from 5 in. at the shell to 18 15/16 in. at the inner face. This aperture facing the electrodes appears to act as an open trap for splash, and a change was made early in June 1950 to improve this condition.

This improvement consisted of raising the charging slot 9 in. above its previous location. In addition to raising the slot, a silicon-carbide arch, which maintains the 5 in. height throughout, was installed. The new slot appears on Fig. 2 and, as can be seen, it overhangs and partially protects the lower sill from splash. The charging delays for jammed cathodes and slot cleaning have been reduced greatly.

The silicon-carbide sill still presents a problem as this material quickly oxidizes. There is apparently a reaction between the oxides of copper and the carbide, as boiling can be seen around the lower edge of the sill. A periclase brick sill will be tried at the next repair, but the furnace has operated successfully for months with little or no sill brick.

**Quality Control of Metal:** Delivery of good quality cathodes leaves control of arc furnace metal dependent on the three elements: Oxygen, sulphur, and iron. This resembles reverberatory practice, but manipulation differs. The three elements are dealt with in order.

The arc furnace is vented by a 9-in. diam circular opening, six courses in from the side of the roof. An open bonnet, a few inches above the aperture is connected to a 5500 cfm fan. Regulation of air entering the furnace is obtained by changing the size of the roof vent with a movable brick cover.

The operators take two samples each hour, one from the arc furnace tap hole and one from the induction unit. The physical laboratory determines oxygen optically on cubes made from the samples and reports the results to the furnace foreman. Oxygen ranges from a trace to 0.02 pct with an ideal of 0.01 pct. The furnacemen regulate the roof vent in accordance with the analyses.

Sulphur could originate from the electrodes, the furnace lining, or the cathodes. Sampling and analysis of each electrode shipment has shown no sulphur. Chemically-bonded magnesite brick contains sulphates. As a result excess sulphur shows up for a time after a repair, but drops rapidly in a few hours; and the sulphur content soon becomes normal.

Sulphur control, therefore, centers on maximum removal of the sulphates and sulphuric acid from

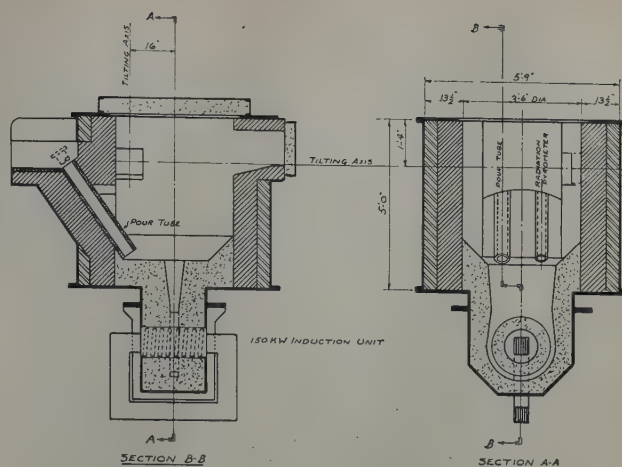


Fig. 3—Induction holding furnace for copper, 5-ton capacity, 100 kva.

the cathodes as they come from the tanks. This, obviously, is a washing problem, and sulphur removal has evolved along the following lines. The tank house has been equipped with twin dip tanks of sufficient size to take a whole lift of 40 cathodes and to allow complete submergence. Operators fill both tanks with fresh water before pulling starts and add 1.5 pt of a sulphate-free detergent to the first, and 1 pt to the second tank. Racks of cathodes are submerged, loops and all in the first tank, and soaked 2 min to dissolve or loosen crystals which may have formed within the loop. After lifting, the rack is held for half a minute to drain, which is the chief function of the detergent as it gives a better run-off. Next is a quick rinse in the second tank and the water sprays on the unloading machine.

Crystalline material within the loop has proved most difficult to eliminate. While the shears cut off the loop and upper 10 pct of the cathode, experience has shown that sulphates, if not removed from the loops in the dip tanks, slowly dissolve and run back over the body of the sheets while still wet.

Iron originates from the same sources as sulphur. It has proved to be negligible in each shipment of electrodes to date. In refractories, iron control becomes more complex. Our experience has been that the iron content of refractories, provided they remain in place in either the hearth, walls, or roof, is not serious. However, iron is absorbed immediately by the bath if it becomes covered with spalled brick.

Chemically-bonded magnesite brick contains upwards of 10 pct total ferrous and ferric oxides. A chrome-magnesite roof, installed in June, carries somewhat more. Similar to sulphur, iron shows up in the first hours after relining. During the present campaign, however, and in spite of the higher iron in the roof brick, the June through September monthly composites contained 0.0015, 0.0012, 0.0014, and 0.0010 pct iron respectively, which are satisfactory values.

**Slag:** Slag formation varies directly with accidental or deliberate additions to the bath. Because of the very refractory character of the furnace lining, the skimmings should not be termed slag, as they consist of semifused crusts impregnated with copper shot and oxides. The analysis of the September skims was: Cu, 21.71 pct;  $\text{Fe}_2\text{O}_3$ , 2.86;  $\text{Al}_2\text{O}_3$ , 3.89;  $\text{SiO}_2$ , 20.00; CaO, 4.68; MgO, 33.28; and  $\text{Cr}_2\text{O}_3$ , 8.90. Ignoring the copper, the remainder corresponds to



an accidental mixture of roof and wall brick plus a minor amount of magnesite cement.

*Operation in General:* Both furnaces operate around the clock, except for one prearranged shut-down each week for repairs. This has gradually evolved as part of the routine and lasts for an hour or so.

The shift foremen enter on a special report delays in the furnace charging and the exact cause therefor. An average of a three-month period in the summer of 1950 indicates 1.6 pct lost time for mechanical breakdowns, 0.2 pct for electrical, 9.2 pct for slot cleaning, and 4.3 pct for operational delays including the weekly planned shutdown.

Copper build-up on the slot remains the largest single source of lost time, and modification of the slot is further projected to overcome the difficulty. Operating delays include slipping or adding electrodes, infrequent stoppages for skimming of the bath, and miscellaneous troubles.

The arc furnace is rated at 20 tons per hr. This rate has not been reached yet over an extended period; the best daily tonnages have been approximately 15 tons per hr, but over shorter periods the rated capacity has been approached.

A low power factor was obtained from the original 20-in. electrodes, and these were changed to 14-in. in December 1949, resulting in a rise in the power factor to over 70 pct. Characteristics of the larger electrodes were current surges, excessive agitation of the bath, a 50 to 60 pct power factor, but comparatively cool side walls and roof at any given bath temperature, and slightly less power consumption per ton melted. The smaller electrodes reduced current surging, and raised the power factor, but the walls and roof were relatively hotter for the same metal temperature, and the electrodes operate at low red heat between the clamps and the roof ring because of increased IR loss.

Electrode consumption in May, August, and September 1950, averaged 3.96, 4.20, and 3.96 lb per ton respectively. The intervening months were higher because weekend shut-downs raised wastage by consuming electrodes during holdovers when no copper was being melted.

*Arc Furnace Power Consumption:* During weekend holdovers in the summer of 1949, it was established that about 300 kw per hr was required to maintain the temperature in a full furnace bath when no cathodes were charged. This constant is the furnace heat loss, and continues at all times; therefore, on a per ton basis it is proportionally more or less according to the casting rate. At 5 tons per hr the loss, expressed as power, would be 60 kw-hr per ton, 30 kw-hr per ton for 10 tons, and 20 kw-hr per ton at 15 tons melted per hr.

According to the best thermal data,<sup>2</sup> molten copper at 2300°F contains 182.8 lb cal per lb, which is equivalent to 192.8 kw-hr per ton. If the heat loss input of the last paragraph is added, it gives 253 kw-hr per ton for 5 tons per hr, 223 for 10 tons, and 213 for 15 tons.

These figures are somewhat low on a current operating basis for two reasons. First, heat losses were based on a new furnace lining and roof, and the caloric loss will be higher with an old lining or thin roof. Second, they were also based on 20-in. electrodes, and as the 14-in. operate at low red heat

above the furnace roof, this IR loss would increase the 300 kw per hr loss. Power consumption currently ranges between 250 and 280 kw-hr per ton melted, depending on the casting rate.

*Temperature Control:* A multiplicity of temperature readings are recorded automatically or read at stated intervals and entered on the shift reports. Three equally spaced, dial, gas thermometers are inserted through the arc furnace shell to contact the brick slightly below the metal line. Under the charging slot, shell temperatures are taken once a shift with a surface-contact thermocouple. A thermocouple is embedded in the brick bottom at the apex of the inverted dome of the hearth. The temperature at this position is also recorded once a shift.

All the foregoing were installed originally to signal bottom failure, and the foremen record the temperatures at the start of each shift. To date, no failure has occurred, and the readings have had little significance. At the end of the last preheating in June 1950, the thermocouple in the bottom of the hearth recorded 320°F, rose to 400° in two weeks, and reached 420° after five months.

A radiation pyrometer with the internal end of the target tube flush with the inner face of the arc furnace wall automatically records the wall temperature. This was installed as a safeguard immediately after observing that the 14-in. electrodes gave significantly hotter walls. The normal range lies between 2400° and 2500°F, but a limit of 2600° was established, and the power input is reduced when temperatures exceed the latter figure.

Arc furnace operators insert an immersion thermocouple in the tap hole every 15 min, and the result is recorded automatically on a chart. Typical readings over any one day would be a maximum of 2380°F, minimum of 2250°, and average of 2310°.

At the induction furnace a second radiation pyrometer, sighted on a tube terminating in the bath, records metal temperatures and automatically controls the power input. This is checked manually once an hour with an immersion thermocouple, and the normal range lies between 2180° and 2250°F.

During a 57-hr layover in 1949, it was established that a power input of 49 kw per hr was necessary in order to hold the induction furnace bath at an even temperature, with neither metal input nor output. The two operating taps are 30 and 65 kw-hr, and theoretical calculations based on the heat loss and a 15 ton per hr at 2300°F input, show that the lower tap would give a constant bath temperature drop of 14°F, and the higher a pick up 6°F. The metal, leaving the induction furnace is, therefore, in the neighborhood of 2200°F.

The function of the core-bushing thermocouple at the primary induction loop has been described. In addition, two gas thermometers are inserted in the cooling-fan discharge of the same bushing, and air temperatures are noted as an extra precaution.

*Dust Loss:* Copper, even at conventional reverberatory temperatures, has a slight vapor pressure, and under the much hotter arc, it becomes appreciable. A wet cyclone treats gases from the roof vent and charging slot. Total vaporization amounts to approximately 4 lb of copper per ton melted, of which the scrubber recovers about 85 pct. The lost fume is largely around one micron in diameter, and a small bag house is in process of being installed to collect it. The recovered dust is recharged into the reverberatories, as it is largely pure cuprous oxide.

<sup>2</sup> U.S. Bureau of Mines, *Bulletin* 371.



# Metallographic Techniques for High Purity Aluminum

by Italo S. Servi and Nicholas J. Grant

**S**PECIAL polishing and etching techniques were developed during an investigation of the high temperature mechanical properties of high purity aluminum (99.995 pct Al).<sup>\*</sup> Electrolytic polishing was done successfully in the following electrolyte: 5 ml perchloric acid (72 pct), and 95 ml glacial acetic acid.

No special precautions need be taken during the preparation of the electrolyte since no appreciable heat of mixing is evolved. Although the electrolyte is not an explosive, it is recommended that Jacquet's safety rules<sup>1</sup> be followed during the polishing operation.

A voltage of 25 to 60 v gives a good polish in about 2 min at room temperature after preparation on 3/0 metallographic paper. Most of the grain boundaries are visible under the microscope after polishing. Since the current is controlled essentially by the resistance of the bath, it is necessary to keep the anode-to-cathode distance as constant as possible.

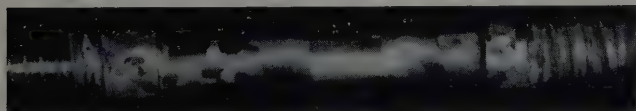


Fig. 1—High purity aluminum. Electrolytic polish and etch as described in text. X15.

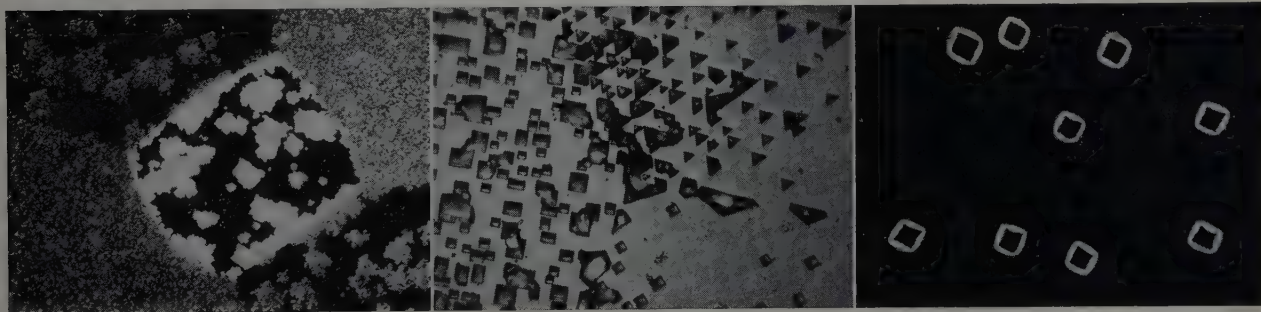


Fig. 2—High purity aluminum. Electrolytic polish in perchloric-acetic acid. a (left)—Partial "galvanic" etching in hydrochloric acid. Polarized light. X50. b (center)—Etched in modified Lacombe

Accordingly, polishing of irregularly shaped pieces will be difficult. A cooling bath and a stirring system are advisable in order to keep the temperature of the bath uniform and constant.

Coarse-grained samples can be macroetched in a few seconds by lowering the voltage below 10 v. This is done after electrolytic polishing, without removing the sample from the bath, Fig. 1. The specimen can be repolished in less than 1 min by raising the voltage above 25 v.

The "galvanic etching" technique, which has

been described elsewhere,<sup>2</sup> was found to be helpful not only for macroetching, but also for microetching coarse-grained specimens. In fact, the different orientations of adjacent grains provide good contrast at the grain boundaries, when the sample is observed under polarized light.

If the specimen is only partially etched, Fig. 2a, the grain boundaries can be located without completely destroying the appearance of the surface of the specimen. The unetched surface appears black under polarized light. Excellent color contrast is obtained by using a "sensitive tint" plate in the optical system of the microscope. In this case, the unetched surface has a magenta color, while the etched part of the sample assumes different colors varying from green to brown, according to the orientation of the grains.

Etch pits were produced on high purity aluminum by using the technique suggested by Lacombe and Beaujard.<sup>3</sup> Good results also were obtained by substituting 70 pct nitric acid for the fuming nitric acid recommended. This gave an etching reagent of the following composition: 70 ml nitric acid (70 pct), 50 ml hydrochloric acid (37.5 pct), and 3 ml hydrofluoric acid (48 pct). An example of the results is shown in Fig. 2b. The outline of the etch pits is revealed sharply if the specimen is observed under

reagent for 30 sec at 9°C. X1000. c (right)—Etched in Lacombe reagent for 30 sec at 9°C. Polarized light. X500. Area reduced approximately 75 pct for reproduction.

polarized light, as shown in Fig. 2c.

These metallographic techniques are not suitable for the examination of commercially pure (2S) aluminum.

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\* The high purity aluminum was kindly furnished by the Aluminum Co. of America.

## Origin of the Cube Texture in Face-Centered Cubic Metals

by Paul A. Beck

THE occurrence of the (100) [100] or "cube" texture upon annealing of cold-rolled copper has been much investigated.<sup>1</sup> The conditions favorable for its formation were found to be a high final annealing temperature<sup>2</sup> or long annealing time,<sup>3</sup> a high reduction of area in cold rolling prior to the final anneal,<sup>2</sup> and a small penultimate grain size.<sup>4</sup> The effects of penultimate grain size and of rolling reduction were found by Cook and Richards<sup>4</sup> to be interrelated in such a way that any combination of them giving lower than a certain value of the final average thickness of the grains in the rolled material leads to a fairly complete cube texture with a given final annealing time and temperature. Also, according to the same authors, at a higher final annealing temperature a larger average rolled grain thickness, i.e., a lower final rolling reduction, is sufficient than at a lower temperature. These somewhat involved conditions can be understood readily on the basis of recent results obtained at this laboratory.

Hsun Hu was able to show recently by means of quantitative pole figure determinations that the rolling texture of tough pitch copper, which is almost identical with that of 2S aluminum,<sup>5</sup> may be described roughly as a scatter around four symmetrical "ideal" orientations not very far from (123) [112]. In the case of aluminum, annealing leads to retention of the rolling texture with some decrease of the scatter around the four "ideal" orientations, and to the appearance of a new texture component, namely the cube texture.<sup>6</sup> A microscopic technique, revealing grain orientations by means of oxide film and polarized light, showed that the retention of the rolling texture is achieved through two different mechanisms operating simultaneously, namely "recrystallization in situ," and the formation of strain-free grains in orientations different from their local surroundings, but identical with that of another component of the rolling texture. Thus, a local area in the rolled material, having approximately the orientation of one of the four "ideal" components of the texture, partly retains its orientation during annealing, while recovering from its cold-worked condition, and it is partially absorbed at the same time by invading strain-free grains of an orientation approximately corresponding to that of another "ideal" texture component. The reorientation here, as well as in the formation of the strain-free grains of "cube" orientation, may be described as a [111] rotation of about 40°, see Fig. 1 of ref. 6. The preferential growth of grains in such orientations is a result of the high mobility of grain boundaries corresponding to this relative orientation.<sup>7, 8</sup>

It appears very likely that in copper the mechanism of the structural changes during annealing is similar to that observed in aluminum (except for the much greater frequency of formation of annealing twins in copper). In both metals the new grains of cube orientation have a great advantage over the

new grains with orientations close to one of the four components of the rolling texture. This advantage stems from their symmetrical orientation with respect to all four retained rolling texture components of the matrix; they are oriented favorably for growth at the expense of all of these four orientations. As a result, the growth of the "cube grains" is favored over the growth of the others, as soon as the new grains have grown large enough to be in contact with portions of the matrix containing elements of more than one, and preferably of all four component textures.

It is clear that this critical size is smaller and, therefore, attained earlier in the annealing process if the structural units, such as grains and kink bands, representing the four matrix orientations are smaller, i. e., if the average thickness of the rolled grains is smaller. Hence, for a given annealing time and temperature, a smaller penultimate grain size and a higher rolling reduction both tend to increase that fraction of the annealing period during which the above condition is satisfied. Consequently, the percentage volume of material assuming the cube orientation increases. The same is true also for increasing time and temperature of annealing when the penultimate grain size and the final rolling reduction are constant, since the average size attained by the new grains during annealing increases with the annealing time and temperature. For the same reason, at higher annealing temperatures a given volume percentage of cube texture can be obtained with larger rolled grain thickness (larger penultimate grain size, or smaller rolling reduction) than at lower annealing temperatures. The well-known conspicuous sharpness of the cube texture may be interpreted as a result of the fact that selective growth of only those grains is favored that have an orientation closely symmetrical with respect to all four components of the deformation texture and exhibit, therefore, a high boundary mobility in contact with each.

The effect of alloying elements in suppressing the cube texture, as described by Dahl and Pawlek,<sup>9</sup> appears to be associated with a change in the rolling texture. For face-centered cubic metals, such as copper, which do exhibit the cube texture upon annealing, the rolling texture is always of the type described above, i. e., scattered around four "ideal orientations" of approximately (123) [112]. The addition of certain alloying elements, such as about 5 pct Zn or 0.05 pct P in copper, has the as yet unexplained effect of changing the rolling texture into the (110) [112] type. This texture consists of two fairly sharply developed, twin related components. In such cases, as in 70-30 brass and in silver, the annealing texture again is related to the rolling texture by a [111] rotation of about 30°, however, because of the different rolling texture to start from, it has no cube texture component. At higher temperatures, both in brass<sup>10</sup> and in silver,<sup>11</sup> grain growth leads to a further change in texture: A [111] rotation of the same amount, but in reversed direction, back to the original rolling texture.

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In summary, it may be stated that the oriented growth theory of annealing textures readily explains, at least qualitatively, the various conditions and their interrelations thus far described in the literature, that affect the formation of the cube texture.

### Acknowledgment

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### Technical Note

## Theory of Annealing Textures

by Paul A. Beck

IN several recent investigations<sup>1-4</sup> considerable evidence was accumulated to show the predominance in various face-centered cubic metals of a certain relative orientation, corresponding to a rotation of 30° to 40° around a  $[111]$  axis, between a matrix with a strong single orientation texture and grains growing in this matrix.\* This relative orientation was found to occur both in recrystallization and in coarsening, "secondary recrystallization", so that one is inclined to look for an explanation applicable in both cases.

The abundance of growing grains in the described orientations proves that suitable "nuclei" are present in the matrix material and that they have the capacity to grow. The scarcity of growing grains in other orientations may be explained in one of two ways. Either the number of nuclei or the rate of growth must decrease strongly for orientations deviating from that predominating among the growing grains, Fig. 1. Both the "oriented nucleation" and the "oriented growth" theory found support in the literature. Because the frequency of nuclei as a function of orientation is in most instances not amenable to direct experimental investigation, a definitive decision is difficult to achieve. However, it is now known with great certainty that the rate of boundary migration is strongly dependent on the relative orientation of the two grains meeting at the boundary and that the orientation favored by high boundary mobility closely corresponds to that predominating in most cases of recrystallization and coarsening.<sup>5</sup> Thus, it was found that, in general, the mobility is very low for boundaries between grains of nearly identical orientation, or for coherent twin boundaries. On the other hand, the boundaries between two grains of a relative orientation corresponding to a  $[111]$  rotation of 30° to 40° have the highest mobility in face-centered cubic metals. If a large variety of nucleus orientations are produced

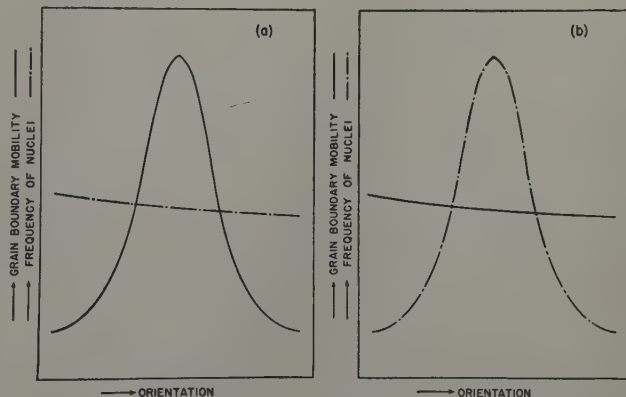


Fig. 1—Grain boundary mobility (solid line) and frequency of nuclei (dotted line) as a function of orientation according to (a) oriented growth theory and (b) oriented nucleation theory.

artificially by means of a highly inhomogeneous local deformation, nuclei close to the above orientation are found to grow fastest.<sup>2-5</sup>

In view of this evidence and of the fact that the preferred orientation relationship is the same in recrystallization and in coarsening, the oriented growth theory appears by far the more promising one. Since the origin of nuclei in primary recrystallization is certainly different from that in coarsening, the occurrence of the same orientation relationship in the two processes would be difficult to explain on the basis of oriented nucleation. Other advantages of the oriented growth theory are its capability of accounting for the often observed sharpening of the texture in coarsening,<sup>6</sup> and its suitability for explaining the role in the formation of the "cube texture" of the most important variables, such as the degree of rolling, the penultimate grain size, and the time and temperature of the last anneal.<sup>7</sup> No similarly consistent explanation of all these effects has ever been offered in terms of oriented nucleation.

An important problem in connection with the oriented growth theory is the following: In the cubic crystal system there are four  $[111]$  axes and

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\* In a hexagonal close-packed metal, zirconium, for which sufficiently good data are available,<sup>12</sup> the reorientation upon recrystallization corresponds to a rotation of 30° around the basal plane normal. Therefore, it may be concluded that in both face-centered cubic metals and in hexagonal zirconium the reorientation in recrystallization corresponds to a rotation around the normal of a close-packed plane. In both cases the new orientation lies about half way between two orientations with low grain boundary energy, where the grain boundary energy may be assumed to have a maximum.

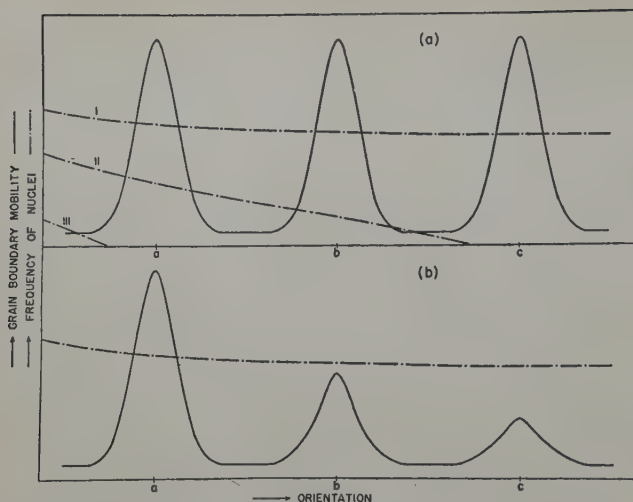


Fig. 2—Grain boundary mobility (solid line) and frequency of nuclei (dotted line) as a function of orientation according to the oriented growth theory. Certain orientations with high boundary mobility do not appear in the texture (a) because of scarcity of nuclei and (b) because the relative maxima of mobility have different values for the various crystallographically "equivalent" favorable orientations.

the  $30^\circ$  rotation around each of these can be carried out in two directions; there are, therefore, eight crystallographically equivalent orientations of the type required by maximum boundary mobility. Out of these, in most cases of recrystallization or coarsening, only one or two actually are observed to occur. The question is then whether it is possible to explain this discrepancy in terms of the oriented growth theory. Let  $a$ ,  $b$ , and  $c$  in Fig. 2a represent schematically three of the crystallographically equivalent orientations with high boundary mobility. If the orientation distribution of nuclei is fairly uniform (line I), all three orientations may be expected to occur in the recrystallization texture. An asymmetrical nucleus distribution (line II), which in itself would not give rise to a well-defined texture in the sense of oriented nucleation (compare with Fig. 1b), might nevertheless give the desired selection from among the eight crystallographically equivalent orientations of high boundary mobility. Another possible answer to the above question is that the orientations  $a$ ,  $b$ , and  $c$  strictly speaking are not crystallographically equivalent, since a deformation texture or a recrystallization texture, no matter how sharply developed, does not possess the symmetry of a corresponding ideal single crystal. Thus, the mobility maxima at  $a$ ,  $b$ , and  $c$  may have quite different values, favoring certain ones among the "equivalent" orientations, Fig. 2b, regardless of nucleus distribution.

It was observed by Burgers and Basart<sup>8</sup> that the recrystallized grains growing in a slightly deformed single crystal of aluminum, in contrast to those formed after heavy deformations, do not exhibit a well-developed texture. The question arises how this behavior can be reconciled with oriented growth. It has been pointed out<sup>5</sup> that the large scatter of orientations in this case may be a result of scarcity of nuclei in all of the orientations favored by high boundary mobility, see line III in Fig. 2a. It is indeed quite probable that an annealing texture does not develop here, because the lack of suitable nuclei prevents oriented growth from becoming operative. This state of affairs in no way affects the general conclusion that annealing textures, when they do occur, are the result of oriented growth.

What is the physical basis for the orientation dependence of boundary mobility? In a previous publication<sup>5</sup> the hypothesis was advanced that the mobility of a grain boundary depends on the rate of self-diffusion along this boundary. Furthermore, it was shown that at least qualitatively the correct orientation dependence of boundary mobility results from this hypothesis, if a plausible assumption is made concerning the rate of grain boundary self-diffusion as a function of the relative orientation of the grains meeting at the boundary. It was assumed that the rate of grain boundary self-diffusion decreases with decreasing grain boundary surface energy, because the atoms at the boundary are more tightly held in their positions. According to this assumption grain boundary self-diffusion is very slow at boundaries where the two grains have nearly the same orientation, and at coherent twin boundaries. This has been experimentally confirmed for tin by Fensham.<sup>9</sup> Analogous results were reported more recently by R. S. Barnes for the grain boundary diffusion of copper in nickel.<sup>10</sup> The above hypothesis, associating grain boundary mobility with the rate self-diffusion along the boundary, also received some independent confirmation recently. D. Turnbull<sup>11</sup> found that the free energy of activation for grain boundary migration in the coarsening of silver is nearly the same as the free energy of activation for grain boundary self-diffusion in the same material. It is quite likely that the elementary processes involved in atomic movements necessary for grain boundary migration are the same as those involved in grain boundary self-diffusion.

#### Acknowledgment

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# Kinetics of Precipitation in Supercooled Solid Solutions

by G. Borelius

**A**BOUT the turn of the century, Gibbs' thermodynamic theory of heterogeneous equilibrium, on the one hand, and the experimental methods of thermal and microscopic analysis, on the other, gave to the physical metallurgist his first scientific tool, the equilibrium diagram. The classical equilibrium diagram of a binary alloy system shows the boundaries between ranges of homogeneous and heterogeneous equilibrium in their dependence of concentration and temperature. A homogeneous solid solution which on cooling passes such a boundary is assumed to precipitate, forming a mixture of two phases with different concentrations.

The equilibrium diagram and the equilibrium theory, however, give no information about the time scheme of the process or the intermediate states passed during precipitation. For this reason it satisfies neither the practical need of the metallurgist nor the curiosity of the physicist. As a matter of fact, in the heat treatment of alloys for technical use the objective very seldom is the equilibrium state. Thus good mechanical properties of construction material are connected, for the most part, with some intermediate state. As these intermediate states are thermodynamically unstable, there is, from a theoretical point of view, always to be expected a decay of the good properties with time; and it is a matter also of practical interest to know whether this natural life time of a material is of the order of, say, ten or thousands of years. Thus, for many reasons, there is a current demand to complete our knowledge of equilibrium through knowledge of the kinetics of the precipitation phenomena. From the point of view of the physicist, the most interesting question in this case is whether there are any general laws governing the kinetics.

According to a generally accepted view, precipitation is ruled by two more or less independent phenomena, the formation of nuclei of a new phase and the growth of these nuclei. It is also commonly accepted that there is a tendency for the velocity of growth to increase with increasing temperature because of the increasing mobility of the atoms. There is also a tendency for the velocity of growth to decrease in the neighborhood of the two-phase boundaries. So far, however, very little is known quantitatively about this fundamental phenomenon in the case of solid metallic systems. In our laboratory attention has been directed especially toward the nucleation phenomena, and a series of measurements have been carried out with the guidance of a work-

ing hypothesis (based on experiences from previous work on order-disorder transformations in alloys) about the influence on the nucleation of thermodynamic potential barriers. However, before discussing the experiments, the theoretical ideas will be considered.

In a binary solid solution the arrangement of atoms on the lattice points approaches with increasing temperature a state of full randomness, as illustrated by the ball model of Fig. 1, that might represent a [111] plane of a face-centered alloy with 30 pct "black" and 70 pct "white" atoms. In reality the atoms are changing places continually with their neighbors so that the picture should rightly have been a moving one. On account of this thermal motion the concentration of black atoms within a certain group of, say, a hundred or a thousand lattice points fluctuates with time around the bulk concentration of 30 pct in a manner governed by statistical laws. With decreasing temperature two independent changes in this state grow more and more important. First, the mobility of the atoms decreases, and second, the forces between the atoms will have an increased influence on the fluctuations. In alloys with a tendency for precipitation, which are the concern of this lecture, the distribution function of concentration fluctuations will broaden, so that the relative probability of great local variations from the bulk concentration increases.

Fig. 2 gives an example of such a fluctuation. When the alloy is supercooled below the solubility limit into the range of two-phase equilibrium, the fluctuations will now and then at some point give rise to a state that resembles the equilibrium state and thus will form a stable nucleus that is capable of growing by diffusion processes. In discussions with colleagues and in the literature, I have often encountered the idea that three or four atoms of the dissolved metal could form a nucleus of the new phase. A look at the ball model might be enough to indicate that this cannot be true. If it were true, there should be nothing but nuclei, whereas we know from experiment that nucleation must be a rather rare occurrence. In fact we have, as will be mentioned later, certain reasons to believe that the nuclei are formed by fluctuations containing some hundreds of atoms, which should be the order of the number of black balls in the fluctuating group of the figure, if it were extended into three dimensions.

As a working hypothesis we have assumed that the fluctuations producing nuclei, though large and rare, still are ruled by the distribution laws of fluctuations of the supercooled solid solution in its initial state. Thus the probability of nucleation will be connected to the thermodynamic properties of the solid

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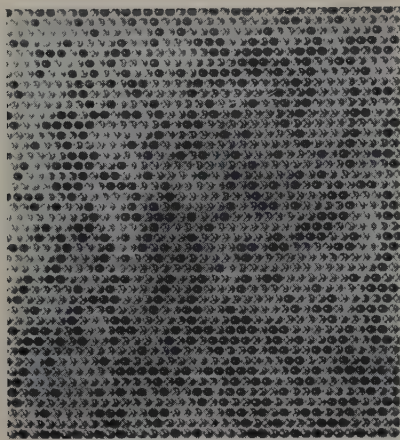


Fig. 1 (left)—Ball model of a 30 pct solid solution with random distribution of atoms.

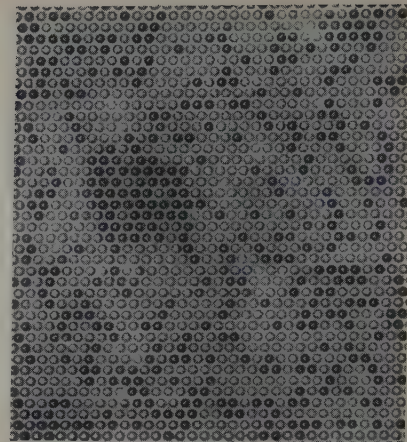


Fig. 2 (right)—Ball model of a big concentration fluctuation in a solid solution.

solution itself. These properties in turn may be determined approximately from the equilibrium diagram, and it is possible to obtain a connection between the equilibrium diagram and the nucleation that might be examined experimentally.

Fig. 3 gives an outline of the theoretical relationships. The upper figure is the equilibrium diagram of a solid binary system such as Au-Pt or Au-Ni with a gap of solubility. The solid line is the limit of solubility. In the lower diagram, the curve  $F$  shows the free energy as a function of the concentration at a certain temperature  $T$ . Between the two contact points of the double tangent, the curve itself gives the free energy of the unstable, supercooled homogeneous solutions, whereas the tangent gives the free energy of the stable mixture of two phases. The part of the free energy that is of importance here may be written approximately:

$$F = U - TS \quad [1]$$

where  $U$  and  $S$ , the structural part of the energy and the entropy, are functions of the concentration  $x$  only, but not of the temperature  $T$ . The entropy is given approximately by:

$$S = R [x \ln x + (1 - x) \ln (1 - x)] \quad [2]$$

whereas  $U$  has to be determined analytically or graphically, so that the contact points of the double tangent at all temperatures fit to the empirical solubility limits.

The theory of fluctuations shows that the distribution of fluctuations is highly dependent on the second derivative of the free energy with respect

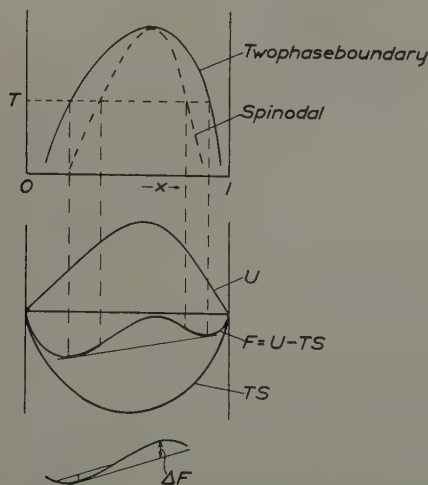


Fig. 3—Thermodynamic relations for a system with limited solubility.

to concentration, that is, on the curvature of the  $F$ - $x$  curve. If this curve bends upward, as it does on both sides within the gap of solubility, the free energy is increased locally by a fluctuation, and as the free energy always tends to a minimum, the fluctuations are repressed, the more the curve is bent. If the curve bends downward, as it does in the central part of the gap, the fluctuations are unrepressed and their distribution is undetermined. A retardation of the fluctuations and accordingly of nucleation therefore might be expected to start above a line, dashed in the phase diagram of Fig. 3, which is the locus of the inflection points of the isothermal  $F$ - $x$  curves. Van der Waals, who in the nineties pointed out this line as the lower limit of metastable equilibrium, called it the spinodal, a name that we will adopt in the following. Above this line the formation of a nucleus presupposes that a group of, say,  $n$  atoms passes a thermodynamic potential barrier, which under certain simplifying assumptions can be expected to be the maximum difference  $\Delta F$  between the  $F$ - $x$  curve and the tangent to the curve at a point corresponding to the concentration of the alloy concerned. The probability of nucleation might be given by the formula:

$$P = P_0 e^{-\frac{Q}{RT}} e^{-\frac{n\Delta F}{RT}} \quad [3]$$

where  $Q$  is the activation energy per mol for the change of place of the atoms. As to the number  $n$ , the theory so far cannot give any prediction either of its magnitude or its dependence on concentration or temperature; it has to be determined from experiment.

The growing nuclei will give rise to new types of

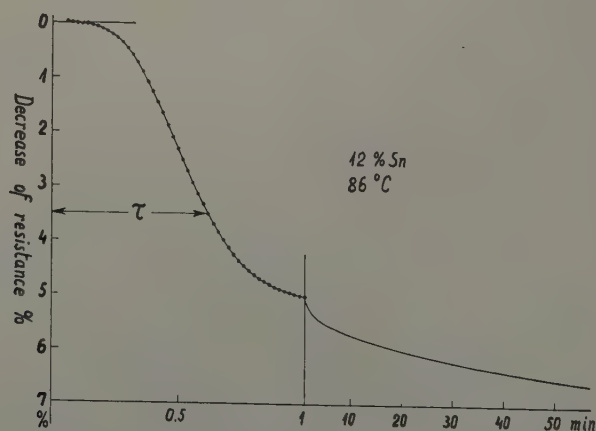
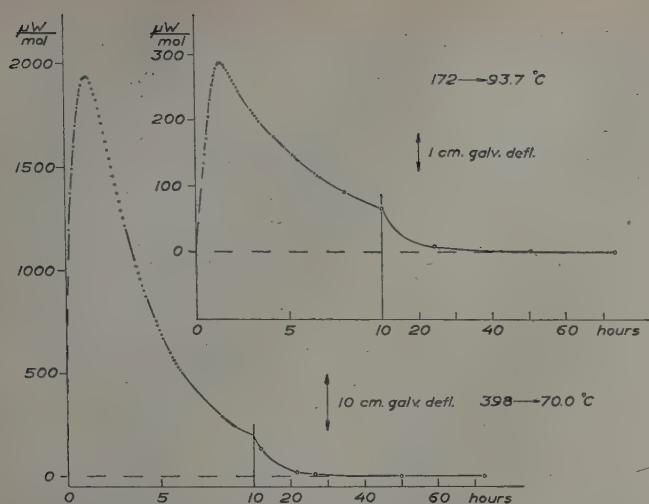
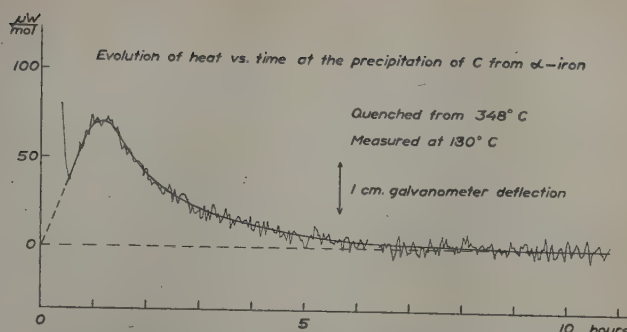


Fig. 4—Decrease of resistance during precipitation in a Pb-Sn alloy.

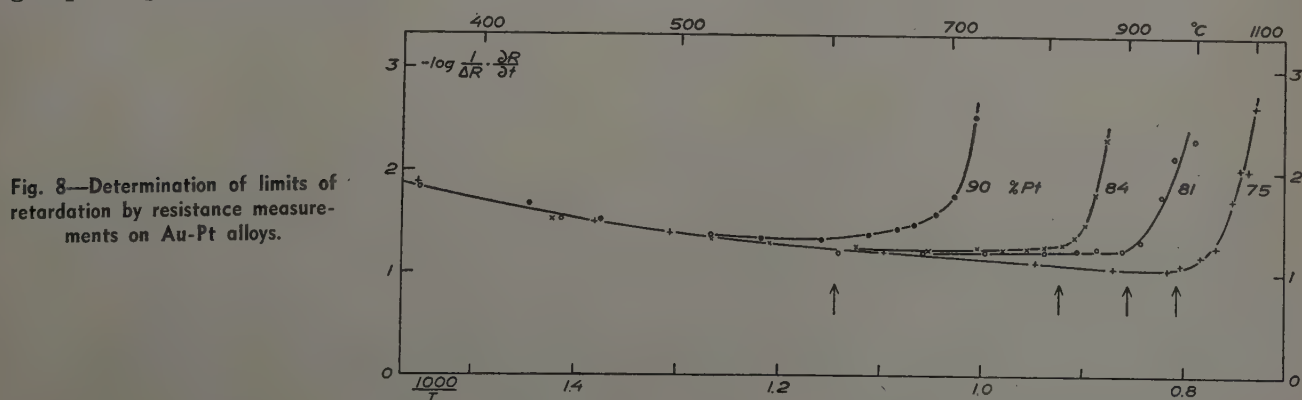




forces in the lattice and corresponding new types of potential energy. Frenkel, Becker, and others have made calculations on the basis of a special surface energy at the surface of the nucleus, and Gorsky, Mott, Nabarro, and others on the basis of internal strain caused by the different atomic distances in and outside the nucleus. In certain cases these strains probably will stop the growth of the nucleus at a submicroscopic size, which at least for the present seems to be a natural interpretation of the submicroscopic age-hardening phenomena. In other cases the nuclei break away from the lattice of the matrix and then are capable of growing by diffusion into crystals of microscopic or macroscopic sizes.



measurements at the temperature of precipitation itself, such as measurements of resistance, magnetic susceptibility, changes of volume, and changes of internal energy, the latter studied by the heat given off from the specimen. In our laboratory two methods have been employed for the most part: Resistometric measurements which are easy and often very useful, especially for the first orientation; and calorimetric measurements, which are less simple to perform, but give results that are more directly interpretable.



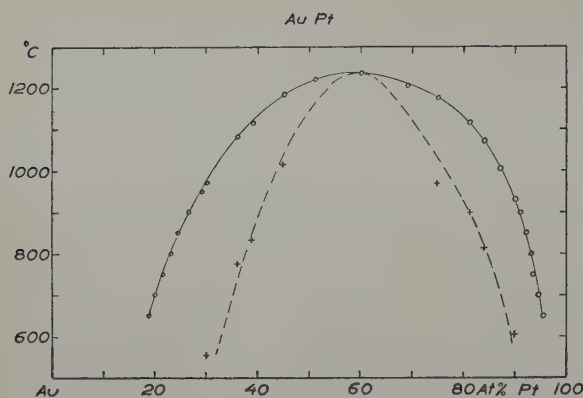


Fig. 9—Solubility limits, spinodal, and limits of retardation in the system Au-Pt.

ing the precipitation of nitrogen dissolved in  $\alpha$  iron. The heat of precipitation is rather small. If after the quenching from 172° to 94°C, the specimen had been insulated thermally, the total increase of temperature caused by the heat of transformation, evolving during some 50 hr, would have been 0.2°C.

Fig. 6 gives an idea of the present limits of the experimental possibilities of the calorimetric method. It describes evolution of heat during the precipitation of carbon from  $\alpha$  iron, ferrite. The specimen had been heated for some time at 348°C, where the solubility of carbon in the ferrite is about 2/10,000 of a percent by weight, and after quenching it was aged at 130°C. This temperature was chosen so that precipitation would be completed in the course of one day, which was the most convenient rate. In this case the specimen, if insulated during the precipitation, would have obtained an increase of temperature of only about 0.02°.

For these investigations we chose those systems of alloys that are simple and of greatest interest;

namely the systems Au-Pt and Au-Ni, which are the only known systems with full mutual solubility at high temperatures, and a gap of solubility at lower temperatures; the system Pb-Sn with a maximum solubility of 30 atomic pct Sn and a precipitation of nearly pure Sn; the system Al-Zn with a broadest range of solubility from 0 to 65 atomic pct Zn, also covering a eutectoid concentration; and the system Al-Cu which, being of great technical importance, has been investigated in many laboratories, so that our results could be compared with those of other investigators. We have also done some calorimetric work on the precipitation of nitrogen and carbon dissolved in  $\alpha$  iron.

The first system investigated in search of influences of thermodynamic potential barriers was the Au-Pt alloys. Results of resistivity measurements by Johansson and Hagsten on an alloy with 30 atomic pct Pt are shown in Fig. 7. Alloys which were cooled rapidly from above the two-phase range gave resistances on a nearly straight line in the resistance-temperature diagram. Further the figure shows the resistances after 1, 5, 10, 20, and 35 hr and after reaching equilibrium. Up to about 550°C the velocity of precipitation increases with the temperature owing to increased mobility of the atoms. Here, 400° below the solubility limit, a retardation sets in which, some 100° below the limit, is so strong that there is no appreciable change in resistance even after 35 hr, although the motion of the atoms must be expected to be very lively at this temperature.

Victorin has investigated a number of Au-Pt alloys in the same way. Plotting the logarithm of the reciprocal of the relative decrease of resistance in 10 min against the reciprocal of the absolute temperature, he obtained curves as shown in Fig. 8 with rather well defined lower limits of retardation.

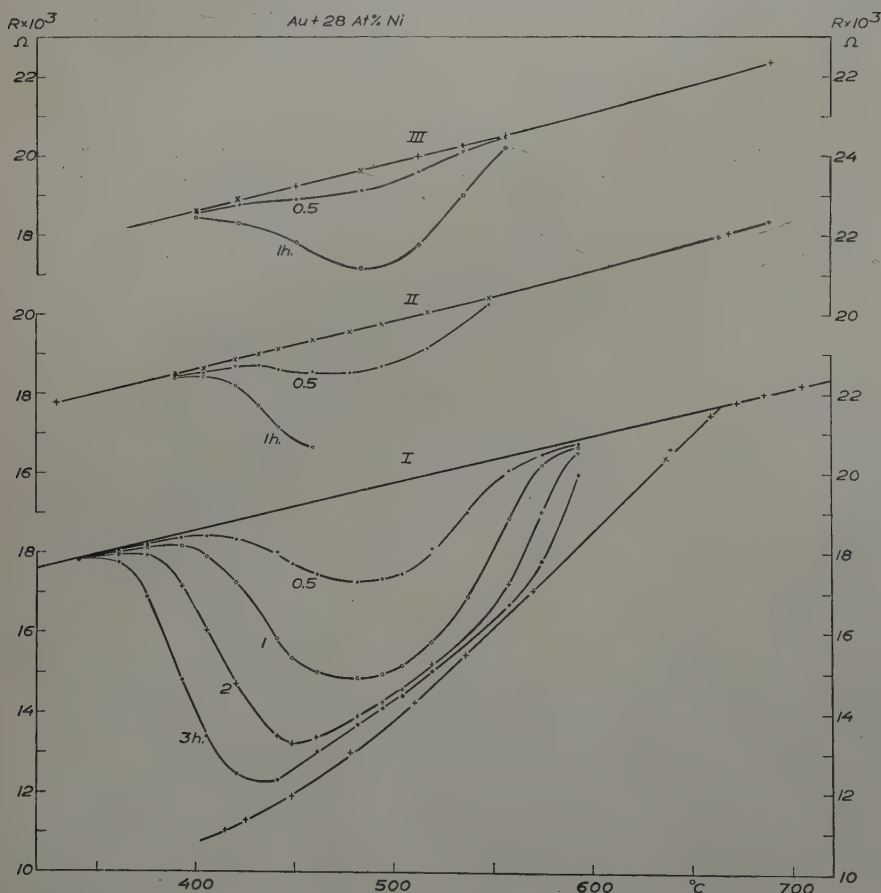


Fig. 10—Decrease of resistance in an Au-Ni alloy with 28 atomic pct Ni during precipitation.



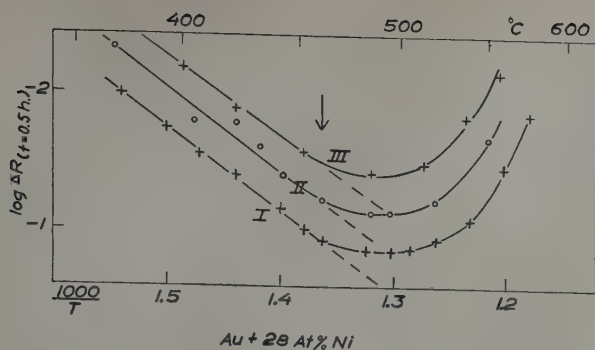
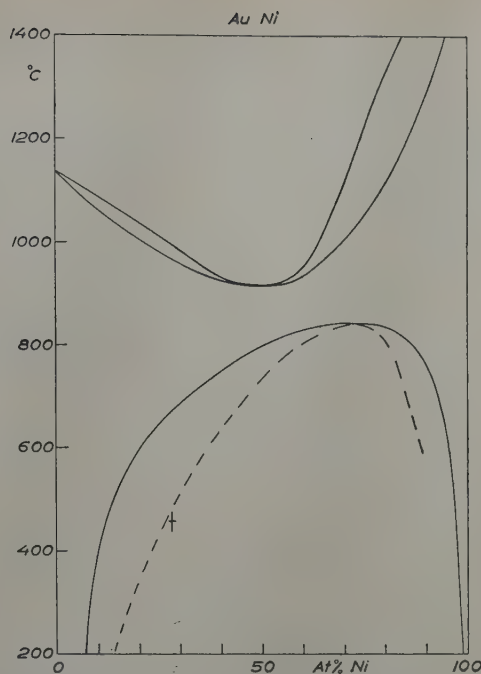


Fig. 11 (above)—Dependence on temperature of the rate of precipitation in an Au-Ni alloy with 28 atomic pct Ni.

Fig. 12 (right)—Solubility limit, spinodal, and limit of retardation in the system Au-Ni.

A careful redetermination of the two-phase boundary, the solid line in Fig. 9, made it possible to calculate the free energy and the spinodal, the dashed line. Within the limits of experimental uncertainty the limits of retardation coincide with the spinodal.

In the system Au-Ni, we have investigated quite thoroughly only one single alloy with 28 atomic pct Ni. A first series of measurements, going from higher to lower temperatures, gave the resistance temperature diagram I of Fig. 10, that was completed by the measurements of the equilibrium state from lower to higher temperatures. A later series, II, showed slower precipitation and a still later one, III, even lower velocity of precipitation. A plot of the logarithm of the reciprocal of the decrease of resistance during the first 30 min against the reciprocal of the absolute temperature, which gives a clearer view of the initial stage of precipitation, is shown in Fig. 11. The three rather parallel logarithmic curves can be interpreted as a sum of the logarithm of a factor decreasing with the increasing mobility of the atoms with increasing temperature, which gives the straight line in the diagram, and the logarithm of a retarding factor. The fact that the curves are parallel to each other in the logarithmic diagram seems to indicate that there are variations in the a priori probability of nucleation between the three states. In fact a



microscopic investigation showed that, at an intermediate stage of the precipitation process, the number of centers of the second phase was very different in different crystal grains. On the other hand, the lower limits of retardation, which appear rather sharply, are the same, about 460°C, in all three cases. Fig. 12 shows how this limit coincides with the position of the spinodal which was calculated from measurements of the solubility limit by Köster and others.

The system Pb-Sn has been studied with resistivity and calorimetric measurements. Fig. 13 shows the logarithm of the time for a decrease in resistance of 2 pct vs. the reciprocal of the absolute temperature for five concentrations. The probable positions of the lower limits of retardation are marked by arrows.

Fig. 14 shows the phase diagram with the experimental limits of retardation marked by crosses. The oblique cross is obtained from a calorimetric investigation. The upper dotted line is the spinodal

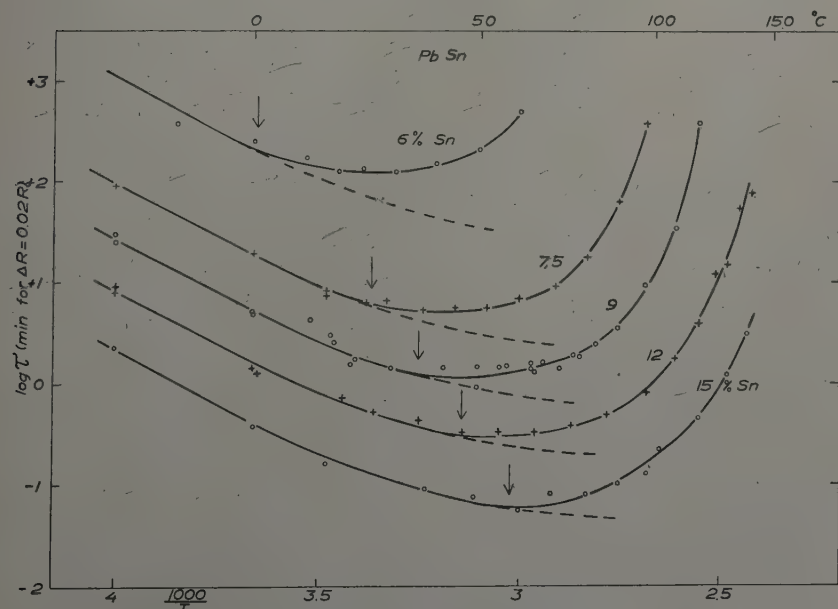


Fig. 13—Logarithms of times for a decrease of resistance of 2 pct vs. reciprocal of absolute temperature for Pb-Sn alloys.

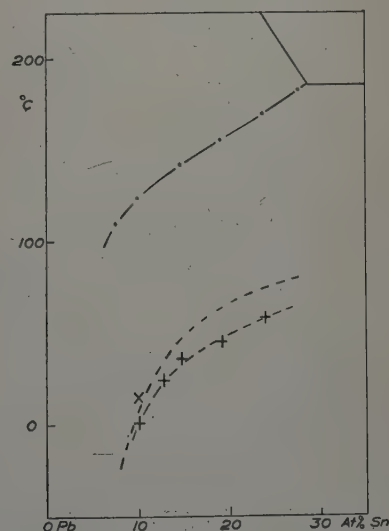
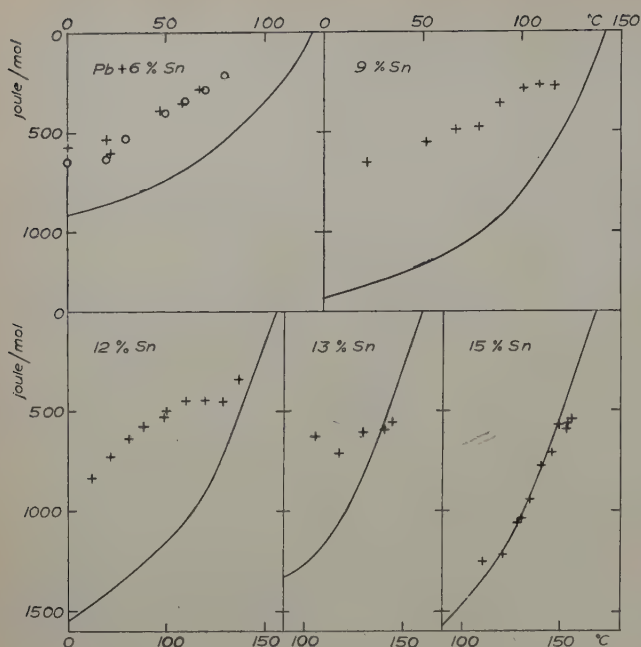


Fig. 14—Limit and solubility, calculated spinodal, and limits of retarded precipitation in the system Pb-Sn.



calculated from the carefully redetermined two-phase boundary. As the available boundary line in this system is rather short, the calculation may be somewhat uncertain.

Calorimetric investigations also have given another type of information. Precipitation above about 100°C has, as shown in Fig. 15, given the total decrease of internal energy that could be expected from the phase diagram, whereas precipitation below 100°C has given only about half of the calculated decrease. There seems to exist below 100°C some intermediate, metastable state, the nature of which we have not discovered so far.

The three systems under discussion have a simple gap of solubility between two primary solid solutions. It was of special interest to try to test the working hypothesis also on a system with a eutectoid point. An imaginable system of this kind with full solubility at high temperatures is shown in Fig. 16, together with free energy curves for the eutec-

Fig. 15 (left)—Calculated and observed total heat of precipitation in Pb-Sn alloys.

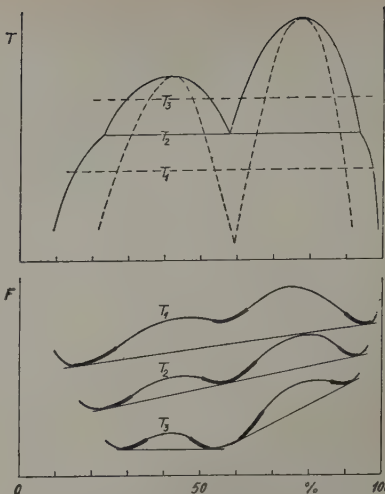


Fig. 16 (right)—Thermodynamic relations for a system with a eutectoid point.

toid temperature  $T_2$ , a higher temperature  $T_3$ , and a lower one  $T_1$ , the parts of these curves for the supercooled solid solutions having a positive second derivative of the free energy are marked with thick lines. The locus of the inflection points, the spinodal, is the dashed line in the upper part of the figure. Although at the lower temperature  $T_1$  there is only one continuous gap of solubility, there are three ranges with positive second derivatives, one of them in the central part of the gap.

Unfortunately there is no known system of this type with an unbroken series of solid solutions at high temperatures. In the system Al-Zn, however, there is at least an unbroken solubility from pure Al to a bit on the other side of the eutectic concentration. In Fig. 17 the solid lines show the two-phase boundaries according to resistometric measurements by Fink and Willey completed by more detailed measurements of our own. The dashed line is the spinodal determined by graphical methods, in this case with some difficulty and uncertainty. The crosses are empirical lower limits of retardation determined by resistivity measurements, and the circles such limits determined by calorimetric investigations. The good agreement with the calculated spinodal may partly depend on good luck, as the results are in fact somewhat complicated.

In this system Guinier has observed at low temperatures a submicroscopic precipitation of the

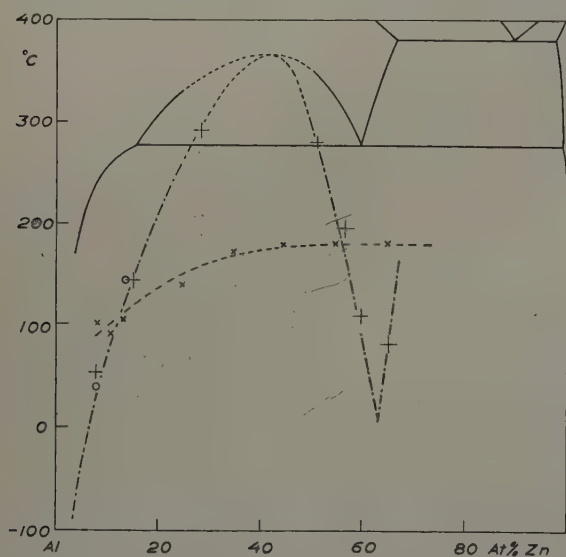
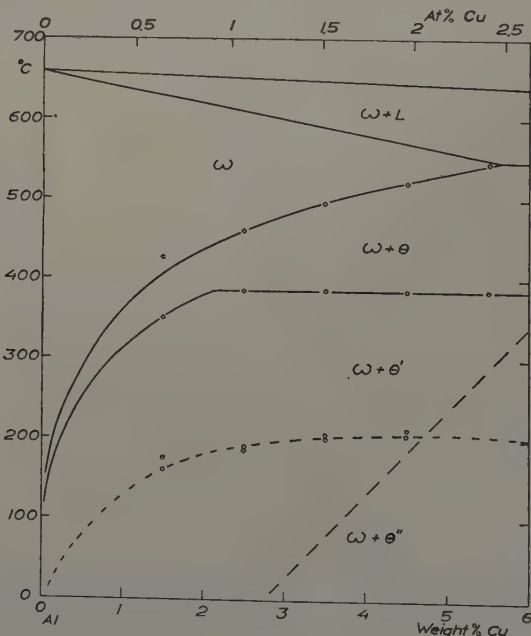


Fig. 17 (above)—Solubility limits, calculated spinodal, lower limits of retarded precipitation, and supposed upper limit of the Guinier-Preston aggregates in the system Al-Zn.

Fig. 18 (right)—Phase limits and calculated spinodal in the system Al-Cu.





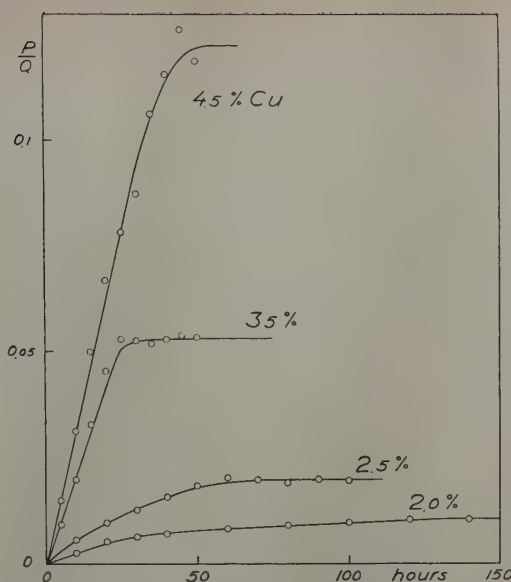
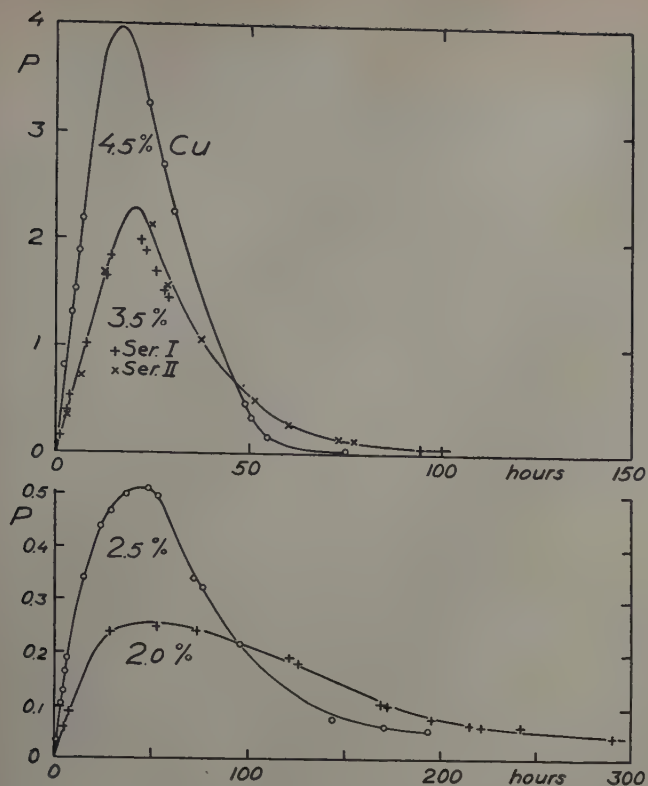


Fig. 19 (left)—Evolution of heat during precipitation in Al-Cu alloys at 225°C.

Fig. 20 (above)—Ratio of power  $P$  to heat  $Q$  still to be given off as a function of time in Al-Cu alloys at 225°C.

Guinier-Preston type. Unpublished results of thermal analysis from our laboratory have shown that homogeneous Al-Zn alloys, which are cooled rapidly and aged at low temperatures when heated at a rate of the order of  $1^\circ$  per min at higher temperatures, show an absorption of heat that was found to start rather sharply at the temperatures marked by oblique crosses in Fig. 17. It is most probable that the line drawn through these points in the diagram is the upper limit of the range of existence of the Guinier-Preston aggregates. It is of particular interest to observe that the retardation of the initial rate of precipitation, governed by the position of the spinodal, appears, as well, within and above this range. From our point of view this is understandable as fluctuations are supposed to be necessary for nucleation in all forms of precipitation.

Another system from which there are kinetic studies of precision to present is the system Al-Cu. The constitution diagram for the Al-side of the system is shown in Fig. 18. Al dissolves up to 5.5 wt pct Cu at  $550^\circ\text{C}$ . There are three known precipitates  $\theta$ ,  $\theta'$ , and  $\theta''$ .  $\theta$  has the composition  $\text{Al}_2\text{Cu}$  and is the stable precipitate at all temperatures below the two-phase boundary.  $\theta'$  is another, metastable, form of  $\text{Al}_2\text{Cu}$  appearing as an intermediate stage of the transformation below about  $385^\circ\text{C}$ .  $\theta''$  is a submicroscopic intermediate precipitate appearing below about  $200^\circ\text{C}$  and causing the well-known age hardening of the Al-Cu alloys. Its nature has been discussed on the basis of X-ray investigations on single crystals by Preston, Guinier, Jagodzinski and Laves, and others. The upper limits of the three states, as shown in the figure, were determined by thermal analysis at rising temperature. The spinodal, as calculated from the two-phase boundary, is represented by the dashed line down to the right in the figure.

In contrast to the alloy systems already reported, we have for the Al-Cu alloys no measurements to report for constant concentrations at varying temperatures crossing the spinodal. They would prob-

ably be rather difficult to perform in this range because of the rapid precipitation. But an attempt has been made to study the influence of the thermodynamic potential barriers on alloys with varying concentrations at three constant temperatures,  $225^\circ$ ,  $110^\circ$ , and  $20^\circ\text{C}$ . The measurements are made by the calorimetric method which is, in this special case, preferable to resistance measurements, the results of which are complicated and difficult to interpret. At  $225^\circ\text{C}$ , we have studied the precipitation of the  $\theta'$  phase in the range of retarded nucleation. The calorimetric power-time curves are shown in Fig. 19. They are of a simple form making it possible to follow the precipitation process from the beginning to the end. The total amounts of heat obtained by integration are, within the limits of the experimental uncertainty, in accordance with the values calculated from the phase boundaries.

For a discussion of the formation of the nuclei, it is convenient to consider, instead of the power  $P$

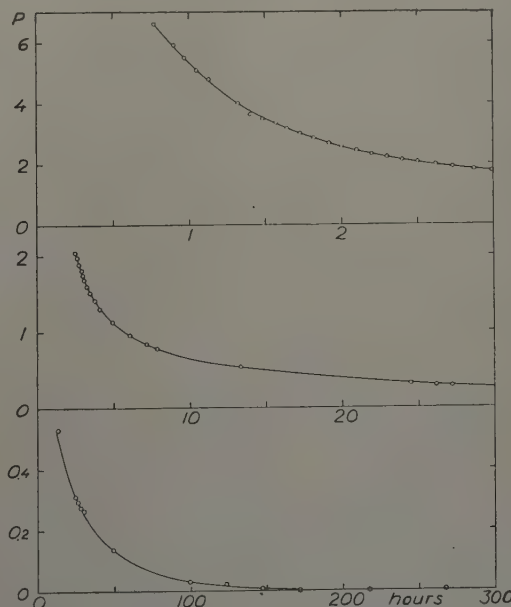
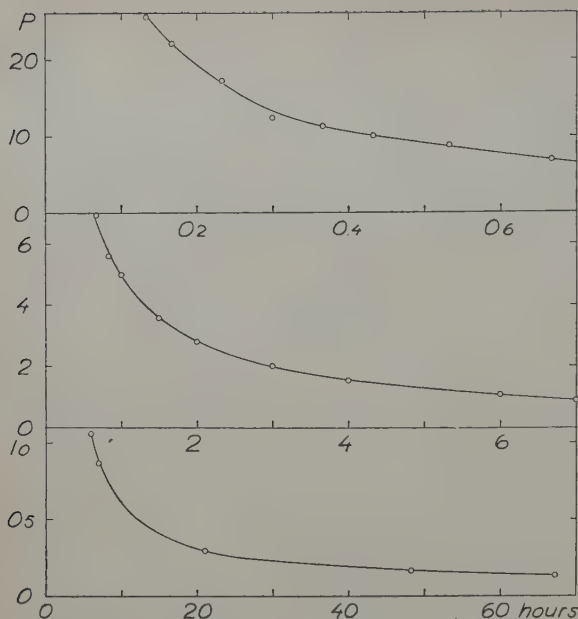


Fig. 21—Evolution of heat as a function of time in an alloy of Al with 4.5 wt pct Cu at  $20^\circ\text{C}$ .



itself, the quantity  $P/Q$ , where  $Q$  is the heat still to be given off.  $P/Q$ , which may also be written  $dQ/Qdt$ , is approximately proportional to the fraction of the atoms still in solution, which per unit of time go over to the precipitate and can be shown to be proportional to the number of nuclei per unit of mass. Fig. 20 gives  $P/Q$  as a function of time. It shows that the number of nuclei first increases linearly and then reaches a constant value. The initial slopes of the curves are relative measures of the probability of nucleation in the supercooled solutions and are, according to eq 3, related to the product  $n\Delta F$  of the number  $n$  of atoms necessary to form a stable nucleus and the thermodynamic potential barrier  $\Delta F$  which can be calculated. In fact we have found good agreement with theory for  $n = 120$ .

The precipitation at 20°C, which is known to give the submicroscopic Guinier-Preston aggregates and which has been studied on samples with concentrations in a range below or near the spinodal, where nucleation is unretarded, give quite another picture in the calorimetric power-time diagram. Because of the unretarded fluctuations and the small distances of diffusion, the first precipitation is so rapid that the concentration of Cu still in solution, which was 4.5 pct in the case of Fig. 21, had decreased to about 2 wt pct before the specimens after quenching had reached the steady state necessary for measurement. What was observed during the measuring series is dependent on the further formation of nuclei, which is more and more retarded as the concentration of the solution decreases and the thermodynamic potential barrier increases. As can be expected under such circumstances, the power-time diagrams, of which Fig. 21 gives an example, take on a hyperbolic form and are not very much different for the various alloys investigated which held from 2.5 to 5.5 wt pct Cu.

The aging at 100°C gives, as is also known from other investigations, a precipitation of the  $\theta'$  as well as the  $\theta''$  phase. The power-time curves, exemplified by Fig. 22, are first hyperbolic like the curves for 20°C but end with an exponential part like the curves at 225°C.

The calorimetric investigations on the precipitation of nitrogen and carbon from solutions of  $\alpha$  iron, of which three examples were given in Figs. 4 and 5,

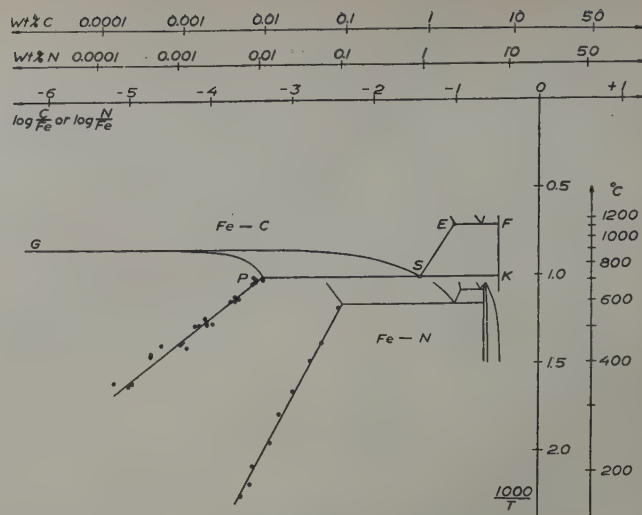


Fig. 22 (left)—Evolution of heat as a function of time in an alloy of Al with 4.5 wt pct Cu at 100°C.

Fig. 23 (above)—Solubility limits in the logarithmic phase diagrams Fe-N and Fe-C.

are so far very incomplete concerning the kinetics of the phenomena. However, the measurements give a new determination of the solubility limits, which is independent of all chemical determinations of the solubility and which might be of some interest of its own.

In the case of nitrogen the evolution of heat was observed at 80° and 94°C in samples which were heated previously at various temperatures from 170° to 575°C in order to obtain equilibrium of solution and thereupon quenched to room temperature. In the case of carbon the measurements were made at 100° or 130°C and covered a range of equilibrium of solution from 350° to 700°C. From the experimental values of the total amount of heat determined at various temperatures, the solubilities may be calculated by means of simple thermodynamic relationships on the assumption that the heat of solubility is constant through the whole range of temperatures covered by our experiments; the accuracy of this assumption, however, for the present is difficult to estimate.

Fig. 23 shows the results on the phase diagrams of Fe-N and Fe-C. Instead of the usual diagrams, with concentration and temperature along the axis, a diagram is used with the logarithms of the atomic ratios N:Fe or C:Fe vs. the reciprocal of the absolute temperature. The advantage of this type of diagram is that the solubility limits for small concentrations approach straight lines.

The results obtained so far seem to indicate that there are besides the phase boundaries two things which have a marked influence on the precipitation and which are fundamental enough to make a part of the phase diagram, namely the spinodal and, at least in some cases, the upper limits of the ranges of existence of various metastable states, as for instance the Guinier-Preston aggregates. It has to be emphasized, however, that the attacks on the problem of understanding the kinetics of precipitation phenomena are still rather fumbling. So, in order to obtain a first simple outlook, we have passed by some important complicating factors, such as the special influences of grain boundaries and cold working and the decreasing rate of crystal growth with decreasing supercooling. Further, our calculations of the free energy from the phase boundaries are only a first rather rough approximation.



# Separation of Copper from Zinc by Ion Exchange

by Ernest J. Breton, Jr. and A. W. Schlechten

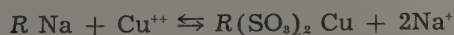
Experiments on the separation of copper and zinc ions by selective action of ion exchange resins showed the carboxylic type to be more effective than the sulphonic resins. The latter demonstrated a greater capacity over a wider pH range. Data show the effectiveness of resins as a means of concentration.

IN recent years the restrictions of stream pollution laws and the high price of metals have created an interest in ion exchange as a means for metal recovery. Some applications have proved successful. In Germany during World War II, 17 tons of copper per day were recovered from rayon mill wastes by means of ion exchange resins;<sup>1</sup> and for some time in this country a large ion exchange unit has been in operation for the recovery of copper from rayon waste water. The possibilities of applying ion exchange to the recovery of metals occurring in plating rinse water is particularly promising.

In most of these applications only the metal being recovered occurs in the waste. The ion exchange resins act merely as a means of concentrating the metals to a point where they can be recirculated. It would be highly desirable to use ion exchange as a means of not only concentrating but also of separating metals. With the exception of the impressive separations accomplished in connection with the atomic energy program, very little has been done on metal separations.<sup>2</sup> Therefore, an investigation was undertaken at the Missouri School of Mines and Metallurgy to determine if either of the two main types of ion exchange resins could be used to separate metal ions in solution. The selective removal of copper ions from a mixture of copper and zinc on carboxylic and sulphonic-type resins was investigated as a function of flow rate, pH, copper-zinc ratio, and concentration. It was shown that zinc can be separated from copper and that very large ratios of concentration can be obtained using ion exchange resins. Since ion exchange is relatively new to the field of metallurgy, a brief review of the subject will be included.

## Theory of Ion Exchange

A comprehensive theory for ion exchange has not been developed as yet, but the mechanisms are analogous to metathetical reactions:



R is the designation for the ion exchange resin. If a copper solution is passed over a resin bed in the sodium form, two ions of sodium will be released for every ion of copper removed. For the most part this reaction follows the laws of mass action and of electrical neutrality. Consequently, if an excess of sodium ions is passed over a bed containing copper,

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the reactions will be reversed, and the resin will be regenerated to its original form.

A few empirical rules governing the exchange reaction have been set forth: 1—In general ions with a high valence will replace ions with a lower valence. 2—Ions having higher activity coefficients have a higher replacement potential. 3—In a series of monovalent ions, those with the smallest radii of hydration will tend to replace those having larger radii of hydration. 4—Where ions are similar in most respects, those with the higher atomic weight sometimes will take precedence. This last rule is not as definite as some of the others. These rules apply to rather dilute solutions at moderate temperatures and assume all ions to be present in about equal concentrations. Higher concentrations and temperatures may in some cases reverse the normal exchange reactions.

Ion exchange materials are unique in that their efficiency increases as the concentration of the solution decreases. For many exchangers, most efficient operation is obtained at concentrations in the order of one thousandths of a percent. Most applications, though, are made in solutions containing considerably higher concentrations than this. Coste<sup>3</sup> has shown that ion exchange resins will remove aluminum and iron effectively from solutions of up to 10 pct chromic acid.

## Ion Exchange Resins

Ion exchange resins are insoluble, porous, resinous structures to which active groups have been attached. Active groups such as  $(-SO_3)^-$  and  $(COO)^-$  pick up cations; hence structures saturated with groups such as these are called cation exchangers. Structures saturated with groups such as  $(-NH_3)^+$  which pick up anions, are referred to as anion exchangers.

The resinous structure of necessity is resistant to strong acids, bases, oxidizing, and reducing agents, and most of the common organic solvents. An idea of the stability can be gaged from the fact that resins last for many years under constant use without detectable chemical or physical breakdown.

The ion exchange reaction is not confined to the surface of these synthetic resins. Its porous structure permits active groups in the center of a particle as well as those on the surface to remove ions. A high capacity resin such as Amberlite IR-120 will remove up to 3.3 lb Cu per cu ft of resin.

In this investigation several approaches to the problem of separating copper from zinc by ion exchange were considered. First, if a reagent could be found which would complex one of these metals and not the other, then by passing this reagent through a bed of exchanger containing copper and zinc, the

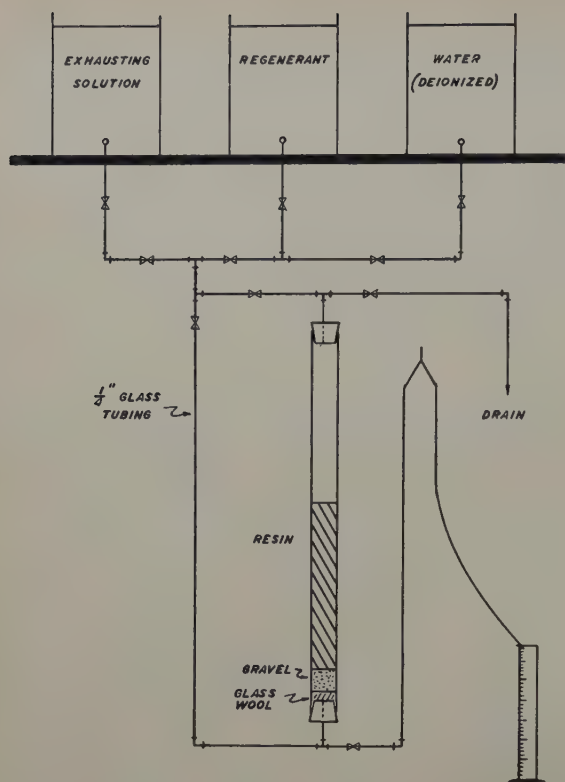


Fig. 1—Laboratory apparatus for ion exchange experiments.

metal that was complexed would be removed selectively. The rare earth metals have been separated in this manner.

Second, if an ion could be found which would replace only one of these two metals on the resin, then a separation could be made by eluting with a solution of that ion.

Third, if either copper or zinc could be complexed to an anion, then that anion could be picked up with an anion exchanger and the remaining cation could be removed with a cation exchanger.

Fourth, if the active groups of an ion exchange resin exhibited a strong preference for copper or zinc, then the two metals could be separated merely by passing a mixture of them through a column of exchanger.

Of these four possible methods for separating copper and zinc, the last one was considered to be the most practical. Accordingly, this study was limited to the investigation of the fractionation of copper and zinc by Method 4 on the two main types of cation exchangers commercially available.

### Equipment and Materials

Fig. 1 shows the apparatus used. The glass column containing the resin was 2.50 cm in diam and 100 cm long. The resin bed was supported by a layer of glass wool covered by 4 in. of 28-mesh Ottawa sand. The tubing and pinch valves were so arranged that the solutions in any of the reservoirs could be delivered to the upper or lower end of the column.

The effluent was removed by first bringing it back up to an open Y above bed level. The open Y served to prevent the bed from siphoning dry if the influent solution should become exhausted.

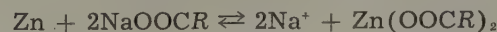
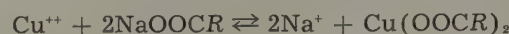
The fractionation of copper and zinc on the two types of cation exchangers, Amberlite IR-120 and Amberlite IRC-50, was studied. Amberlite IR-120 is a high capacity nuclear sulphonic-acid type ion ex-

changer, produced in the form of bead-like particles. It can withstand strong acids and bases even at high temperatures.

In this investigation Amberlite IR-120 was used in the hydrogen form. The sodium form of the resin was converted to the hydrogen form by treatment with 10 pct sulphuric acid. The exchange reaction with copper and zinc for this resin is:



Amberlite IRC-50 derives its exchange activity from carboxylic acid groups. It exhibits exceptionally high capacities in basic solutions and is regenerated efficiently with acids. This resin is supplied in the hydrogen form. On conversion to the sodium form it undergoes up to 100 pct expansion. To allow for this expansion the conversion from the hydrogen to the sodium form was accomplished by stirring sodium hydroxide into a slurry of resin and water. Since the hydrogen form of Amberlite IRC-50 has a slow exchange rate, several hours were allowed for equilibrium to take place. The exchange reaction with copper and zinc could be represented as:



### Procedure

Ion exchange operations are very simple since a run usually consists of only four steps: Exhaustion, regeneration, rinse, and backwash. This procedure was followed in all experiments.<sup>4-6</sup>

A typical experiment involved: 1—Exhaustion: The influent, consisting of an aqueous solution of copper and zinc, was passed through the column until the breakthrough point was reached; that is, the point at which traces of copper or zinc began to appear in the effluent. Periodic qualitative analyses were made to determine this point. After the breakthrough, the run was continued and the effluent was analyzed for copper and zinc. The curve resulting from a plot of zinc and copper concentration vs. volume of effluent was used to evaluate fractionation. These effluent curves will be discussed in some detail later. 2—Regeneration: The copper and zinc were removed from the saturated resin by passing a suitable amount of regenerating solution through the bed. With Amberlite IR-120, 10 pct sulphuric acid was used as the regenerant. Amberlite IRC-50, due to its inefficient exchange of copper for sodium, was regenerated in two steps. First, the copper and zinc were removed with 10 pct sulphuric acid and then the resin was converted back to the sodium form with 4 pct caustic. 3—Rinse: Water was passed through the bed until no more regenerant ions appeared in the effluent. 4—Backwash: In order to reclassify the resin and remove foreign matter, water was passed upflow through the column for 10 min. The flow rate was regulated to give a 75 pct bed expansion. The resin then was ready for the next cycle.

A colorimetric method of analysis was used for copper. For zinc the potassium ferrocyanide method employing uranyl nitrate as an external indicator was used.<sup>6</sup> Distilled water was employed for all backwashing and rinsing operations.

### Experimental Results

The separation of copper from zinc using both resins—Amberlite IRC-50 and Amberlite IR-120—



was studied as a function of: 1—Flow rate, 2—pH, 3—concentration, and 4—copper-zinc ratio. In the study of these variables, the sodium form of Amberlite IRC-50 and the hydrogen form of Amberlite IR-120 were used.

One of the most promising features of ion exchange is the high ratio of concentration which can be achieved. To demonstrate this a 0.005 N  $\text{CuSO}_4$  solution was concentrated on the carboxylic resin.

*Amberlite IRC-50 vs. Amberlite IR-120:* A very good fractionation of copper and zinc on the carboxylic resin, Amberlite IRC-50, was achieved. On the sulphonic resin, Amberlite IR-120, only a slight fractionation was obtained. In Figs. 2 and 3 the effluent curves for these two resins are given.

All of the zinc and copper were removed from the influent, and the sodium that was liberated passed on through the column. The amount of sodium appearing in the effluent was equivalent to the sum of zinc plus copper in the influent. As more influent passed over that part of the resin already exhausted, the copper in solution displaced the zinc. The displaced zinc then passed down the column and reacted with the first sodium resin with which it came in contact. This resulted in banding of the copper and zinc.

After 16 liters had passed through the column, the zinc had reacted with all of the sodium form of the

resin. The column was then divided into two bands, the upper half contained copper and the lower zinc. This was visible inasmuch as the copper color on the resin had progressed only half way down the column when zinc first appeared in the effluent.

When the resin became saturated with zinc, further zinc entering the column plus that displaced by the copper appeared in the effluent. The stoichiometric displacement of zinc by copper was evidenced by the fact that the zinc in the effluent at 22 liters was equal to the sum of the zinc plus copper in the influent. At 42 liters the column contained mostly copper—94 pct. Beyond 42 liters practically no further reaction took place between the influent and the resin.

The exchange mechanism for the sulphonic resin, Fig. 3, was similar to that of the carboxylic resin; however, both ions traveled down the column at approximately the same rate.

To evaluate these effluent curves quantitatively, the percentage recovery and percentage purity of zinc in the effluent was plotted against effluent volume. To arrive at the percentage recovery and purity, the areas under the effluent curves were measured and multiplied by an appropriate factor to give the grams of metal appearing in the effluent. Knowing the influent volume and concentration, the percentage recovery and purity could be calculated at any given volume. Thus:

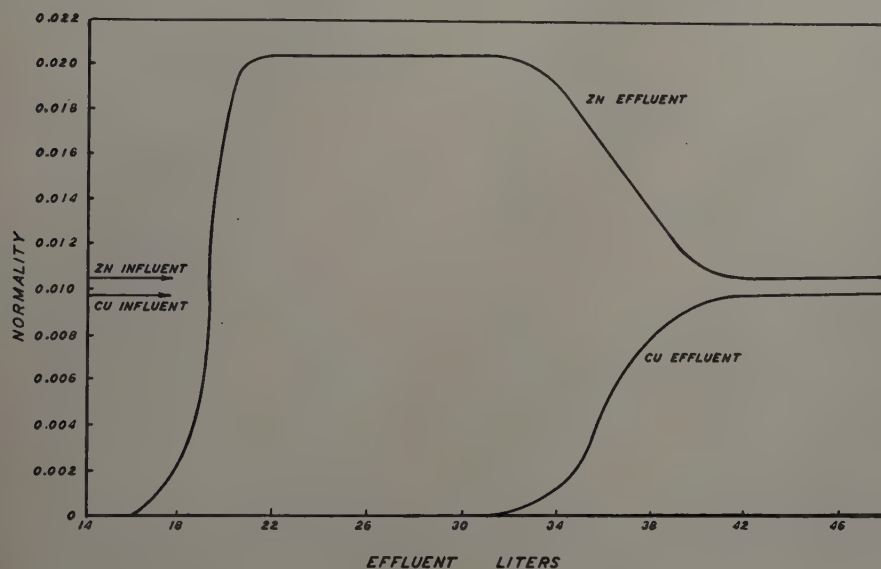
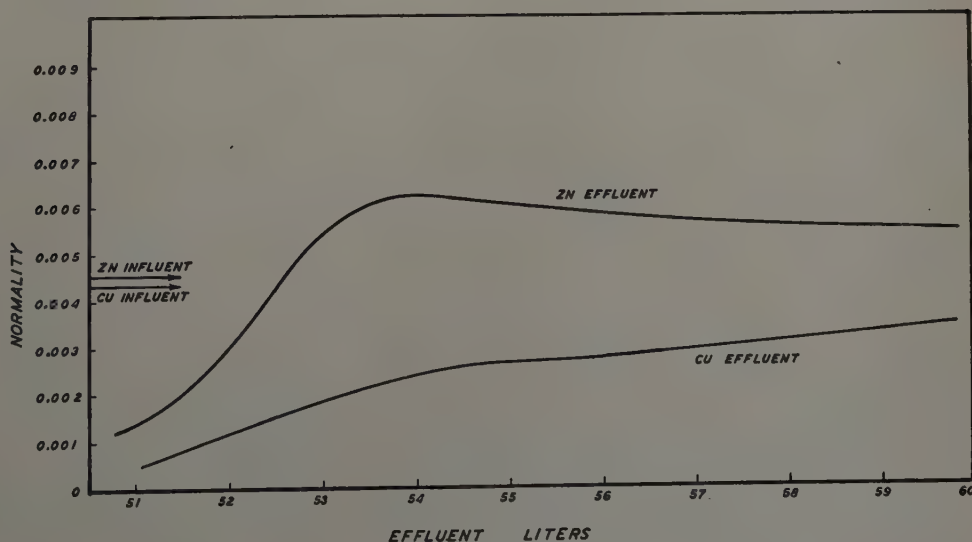


Fig. 2—Fractionation of copper and zinc on Amberlite IRC-50, sodium cycle. Flow rate 0.005 ml per ml resin per min.

Fig. 3—Fractionation of copper and zinc on Amberlite IR-120, hydrogen cycle. Flow rate 0.11 ml per ml resin per min.



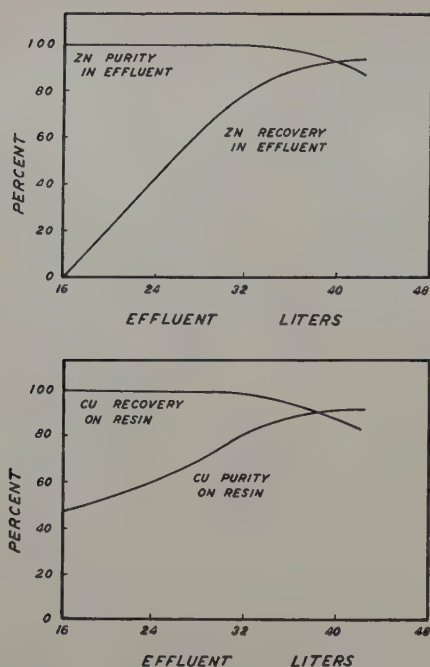


Fig. 4—Separation of copper and zinc on Amberlite IRC-50, expressed as percentage purity and recovery vs. volume of effluent.

$$\text{Recovery} = \frac{\text{Zinc recovered in effluent}}{\text{Total zinc to column in influent}} \times 100$$

$$\text{Purity} = \frac{\text{Zinc in effluent}}{\text{Zinc} + \text{Copper in effluent}} \times 100$$

In Fig. 4 the fractionation of copper and zinc on Amberlite IRC-50 is expressed in terms of zinc recovery and purity in the effluent. The effectiveness of this carboxylic resin in separating copper from zinc is indicated by the fact that 92 pct of the zinc was recovered in the effluent at a purity of 94 pct. Just as the purity and recovery of zinc in the effluent was increased, so the purity of the copper retained on the resin was increased over that in the influent. These results indicate that the carboxyl groups of Amberlite IRC-50 show a great preference for copper over zinc.

Amberlite IR-120 brought about a slight enrichment of zinc in the effluent. Apparently the sulphonic groups of this resin exhibit only a slight preference for copper.

Except for the effect of pH, the ensuing discussion will be limited to the performance of Amberlite IRC-50.

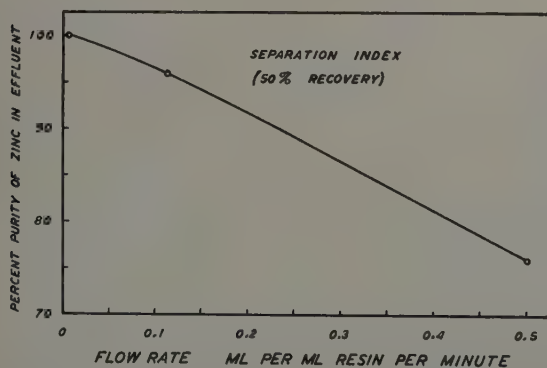


Fig. 5—Effect of flow rate on separation. Amberlite IRC-50, sodium cycle.

**Effect of Flow Rate:** The flow rate had a great effect on both the fractionation and capacity of the resin. The effectiveness of Amberlite IRC-50 was reduced at higher flow rates. In Fig. 5 the decrease in fractionation due to an increase in the flow rate is illustrated. The separation index used in this figure represents the percentage purity of zinc in the effluent when 50 pct of the zinc had been removed from the column. At a flow rate of 0.005 ml per ml of resin per min, a high degree of fractionation was obtained.

An increase in flow rate also impaired the capacity. At a flow rate of 0.1 ml per ml of resin per min the capacity was 0.22 g Cu per ml of resin compared to a capacity of 0.41 g Cu per ml of resin at a flow rate of 0.005 ml per ml of resin per min.

The effect of flow rate is due to the slow reaction rate between the carboxyl groups and copper and zinc. At high flow rates the copper and zinc ions are rushed through and do not have time to approach equilibrium conditions.

**Effect of pH:** Changes in pH had little effect on the fractionation of copper and zinc. It did, as mentioned, greatly affect the capacity of Amberlite IRC-50. In Fig. 6 the effect of pH on the two resins is illustrated. The effect of pH on Amberlite IR-120 was observed by varying the pH of the solution passing through the resin. With Amberlite IRC-50 the pH was varied by titrating NaOH into the acid form of the resin until the desired pH was reached. The influent pH was 5.0 in all cases. These curves mean

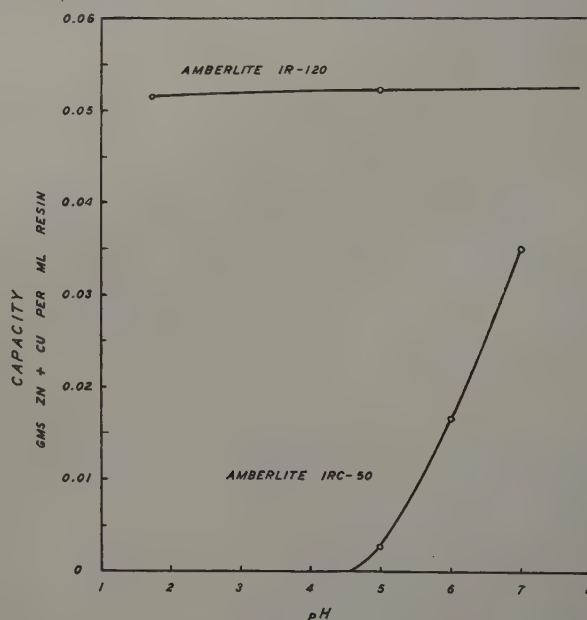


Fig. 6—Effect of pH on capacity

that Amberlite IR-120 can be used effectively at a pH down to and below 1.75. Amberlite IRC-50 on the other hand is very sensitive to pH. To treat solutions with a lower pH, this carboxylic exchanger should be fully regenerated using caustic. Amberlite IRC-50 acts like a weak acid; consequently it has a very high affinity for hydrogen ions. Amberlite IR-120 acts like a strong acid which is highly ionized; its affinity for hydrogen is low.

**Effect of Concentration and Copper-Zinc Ratio:** At a copper to zinc ratio of 1:1, variation in total concentration of copper and zinc between 0.01 and 0.1 normal had no effect on the fractionation of copper and zinc. Below a normality of 0.01 the fractionation,



if any change occurs, should improve. At what concentration above 0.1 normal the efficiency of the resin falls off was not determined.

The copper-zinc ratio, however, had a decided effect on the fractionation. Below a copper to zinc ratio of 1:1, copper was removed effectively from a solution of copper and zinc. On the other hand, as the ratio of copper to zinc increased above one, the complete removal of copper became more difficult. The good fractionation obtained at lower copper-zinc ratios indicates that it would be possible to remove traces or small amounts of copper from stronger solutions of zinc.

### Exchange Resins as Concentrators

The experiment to demonstrate exchangers as concentrators was made by passing an 0.005 N  $\text{CuSO}_4$  solution over a bed of Amberlite IRC-50 until the copper breakthrough in the effluent was reached. A 40 pct  $\text{H}_2\text{SO}_4$  eluting solution then was passed through the column and analyzed for copper. The elution curve is given in Fig. 7. Shortly after 100 cc of eluting solution had passed through, the solubility of  $\text{CuSO}_4$  was exceeded which resulted in the precipitation of  $\text{CuSO}_4$  in the ion exchange bed. The gradual decrease in concentration of copper towards the end of the elution probably was caused by the copper sulphate crystals going back into solution.

The ratio of concentration vs. percentage recovery for this experiment is given in Fig. 8. When 90 pct of the total copper had been recovered in the effluent,

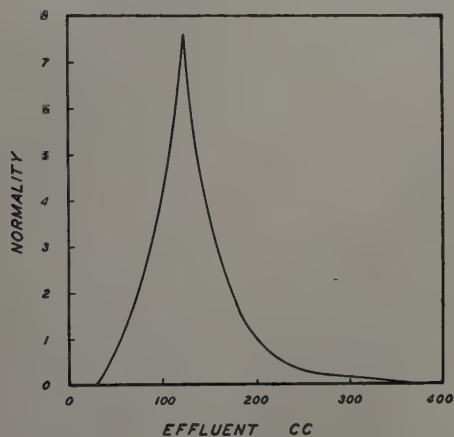


Fig. 7—Elution of copper from Amberlite IRC-50 using 40 pct  $\text{H}_2\text{SO}_4$ .

the volume ratio of concentration was 625.

The high avidity of Amberlite IRC-50 for hydrogen ions makes very high ratios of concentration such as this possible. The regeneration efficiency using acids approaches 100 pct in most cases. That is, almost 100 pct of the hydrogen ions in the regenerating solution contribute to the replacement of copper ions on the resin. On the sulphonic type resins approximately 35 pct of the hydrogen ions in an acid regenerating solution are actively engaged in the exchange reactions.

### Conclusions

It is possible by means of ion exchange resins to remove metal ions from very dilute solutions and recover them in a concentrated form. This suggested the use of ion exchange in metallurgical recoveries. A survey of the literature revealed that little had been done in applying ion exchange to metallurgical problems. Although removal of ionic impurities has been investigated extensively in connection with

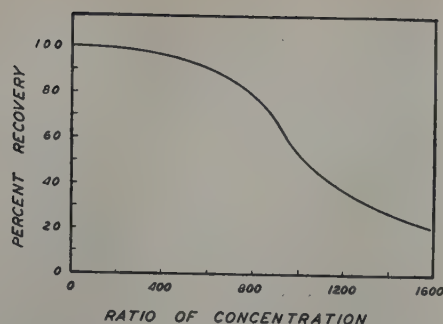


Fig. 8—Ratio of concentration vs. recovery with Amberlite IRC-50 used as a concentrator.

water softening, only limited work has been done on metal separations.

Since the metallurgist is concerned with the separation of metals as well as their concentration, an investigation of the selectivity of ion exchange resins was undertaken. The results of this work on the separation of copper from zinc may be summarized as follows:

1—A carboxylic-type resin can be used to effect the recovery of copper from a mixture of copper and zinc ions. The capacity of this type of resin was very high above a pH of 7; however, below a pH of 5 the capacity became too low for most uses. Consequently, the carboxylic resin would be advisable where a separation is desired.

2—A low degree of selectivity was obtained on the sulphonic resin. It did exhibit a high capacity under wide variation of pH and flow rates; therefore, this type of resin would be useful for the removal of ions under acidic conditions.

3—Ion exchange resins, especially the carboxylic type, can be used to concentrate ions from very dilute solutions.

It appears that there are several possible uses for ion exchange resins in metallurgy. They seem particularly suited to the recovery of metal ions from waste waters. Not only would the recovered metal be of value, but stream pollution could be prevented and possibly the water could be reclaimed.

What role ion exchange will play in the metallurgical field remains to be seen. It seems likely that through this unit process the range of metal recovery can be extended far beyond that obtainable by conventional methods.

### Acknowledgment

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# Ignition Temperatures of Magnesium And Magnesium Alloys

by

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and

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A simple reproducible method was developed for determining the ignition temperatures of magnesium and magnesium alloys and by this method magnesium and over 100 magnesium alloys were measured. The ignition temperature of magnesium was determined in  $O_2$ - $SO_2$ ,  $O_2$ - $N_2$  mixtures and in  $O_2$  from 0.166 to 10 atm pressure. The ignition temperature of magnesium is generally lowered by alloying and increased by an increase in oxygen pressure.

WITH the expanded use of magnesium alloys in industry, ignition temperatures are of considerable importance, especially in heat treating and for service at elevated temperatures. Magnesium alloys exhibit a relatively slow linear oxidation rate up to temperatures near the melting point.<sup>1</sup> At some critical temperature the rate of oxidation becomes extremely rapid. This high rate of oxidation is accompanied by the emission of light and additional characteristics suggesting a flame.

The literature concerning the ignition temperatures of magnesium and magnesium alloys is relatively incomplete and the values reported by various authors are not in agreement. The most probable reasons for this are: 1—The absence of a suitable definition of ignition, and 2—the need of a standardized method of determining the ignition temperatures of inflammable metals and alloys.

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The exact date of the discovery of the fact that magnesium will ignite and burn is unknown. It is likely that H. Davey encountered this property of the metal during its preparation in 1808. The first reference in the literature specifically on ignition of magnesium is by Lenze, Metz, and Rubens.<sup>2</sup> They investigated the inflammability of certain magnesium alloys. Brown<sup>3-4</sup> reported that magnesium ribbon will ignite in air at 507°C by what was called the rising temperature method. Hartman, Nagy, and Brown<sup>5</sup> reported that magnesium powder ignites from 475° to 560°C depending on particle size. According to Guise, Mars, and Wilson<sup>6</sup> prolonged heating in air at 427°C of common casting magnesium alloy causes it to ignite. Samples of magnesium alloys were placed directly in the flame of a torch by Carapella and Shaw.<sup>7</sup> These investigators obtained some evidence of melting prior to ignition. For commercial magnesium, they reported an ignition temperature of 650°C. Their values varied from 450° to 800°C for magnesium alloys. Willmore and Peterson<sup>8</sup> studied the effect of air velocity, humidity, rate of heating, and foreign metal contact on the ignition temperature of magnesium. They conclude that melting is not a prerequisite for ignition and that the conditions which influence ignition are complex and difficult to analyze.

The only quantitative theoretical treatment of the ignition temperatures of magnesium and magnesium



alloys is that of Eyring and Zwolinski.<sup>9</sup> Following the ideas set forth by Pilling and Bedworth<sup>10</sup> in their discussion of the ignition of calcium metal, Eyring and Zwolinski concluded that a metal sample will ignite if the conduction of heat through the oxide film is insufficient to remove the heat produced at the metal oxide interface as a result of the oxidation reaction.

Actually, Constable,<sup>11</sup> Suzuki,<sup>12</sup> and others have shown that this condition exists at temperatures below the ignition temperature.

Eyring and Zwolinski state that as a result of inadequate loss of heat through the film, the temperature at the metal-oxide boundary will increase, accelerating the rate of the reaction. The progressive acceleration of the rate of oxidation will result in the vaporization of magnesium with subsequent ignition of the metal vapor.

The thermal energy lost by conduction from the sample can be equated to the thermal energy produced by the oxidation of the sample. This relationship is expressed by the equation:

$$\kappa \frac{(T - T_0)}{d} = \frac{\Delta H}{N} v \quad [1]$$

where  $\kappa$  is the thermal conductivity,  $v$  is the rate of oxidation,  $T$  is the temperature at the metal-oxide interface,  $T_0$  is the temperature at the outer surface of the film,  $d$  is the thickness of the oxide film,  $\Delta H$  is the heat of formation, and  $N$  is Avogadro's number. According to the proposed theory<sup>9</sup> ignition will occur at the instant the thermal balance represented by eq 1 is destroyed.

The reaction rate,  $v$ , from the Theory of Absolute Reaction Rates<sup>13</sup> may be written as:

$$v = C_s \frac{kT}{h} e^{-\epsilon/kT} \quad [2]$$

where  $C_s$  is the number of adsorption sites on metal atoms per sq cm,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $T$  is the temperature °K,  $\epsilon$  is the activation energy. Substituting eq 2 in eq 1 it becomes:

$$\kappa \frac{(T - T_0)}{d} = C_s \frac{kT}{h} e^{-\epsilon/kT} \frac{\Delta H}{N} \frac{AM}{AF} \quad [3]$$

where  $AM/AF$  represents a roughness factor. Rewriting eq 3 in a more convenient form:

$$T_0 = \left( 1 - C_s \frac{kd\Delta HF}{\kappa h N} e^{-\epsilon/2T} \right) T \quad [4]$$

and substituting in the following values in eq 4:

$$\begin{aligned} C_s &= 1.1 \times 10^{15} \text{ Mg atom per sq cm} \\ k &= 1.38 \times 10^{-16} \text{ ergs per } ^\circ\text{K} \\ \Delta H &= 146 \text{ kg-cal per mol} \\ F &= AM/AF = 16 \\ h &= 6.62 \times 10^{-27} \text{ erg sec} \\ \kappa &= 2.8 \times 10^{-4} \text{ cal cm } ^\circ\text{C}^{-1} \text{ cm}^{-2} \text{ sec}^{-1} \\ N &= 6.02 \times 10^{23} \text{ atoms per mol} \\ E &= 42.7 \text{ kg-cal per mol for 1.78 pct Al-Mg alloy, from ref. 1.} \\ E &= 50.5 \text{ kg-cal per mol for Mg from ref. 1.} \end{aligned}$$

Eyring and Zwolinski calculated the values for the ignition temperature of magnesium shown in Table I.

Thus, the theory of Eyring and Zwolinski indicates that the ignition temperature is dependent on

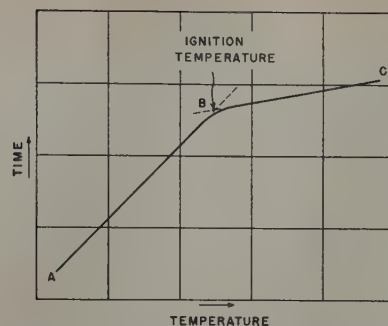


Fig. 1—Typical ignition temperature determination.

the oxide film thickness. As will be shown later, this theory does not agree with the experimental results obtained by the authors in that the time delay experiments indicate that the ignition temperature of magnesium is independent of the nonprotective oxide film thickness. In addition, the thermal equilibrium represented by eq 1 is violated at temperatures below the ignition temperature. The Constable effect would be impossible under the imposed conditions of this equation. As will be shown later, this theory does not explain satisfactorily the experimentally observed fact that the ignition temperature of magnesium is pressure dependent.

From the literature pertaining to the ignition temperatures of magnesium and magnesium alloys, as cited above, it is obvious that none of the experimental values agree and that there is some conflict as to the exact definition of the ignition temperature.

### Experimental Procedure

In this investigation, the ignition temperature is defined as the "explosion temperature," that is, the temperature at which the rate of oxidation suddenly becomes extremely rapid and a "flame" appears. From preliminary experiments it was found that the following method was satisfactory for determining the ignition temperature of magnesium and magnesium alloys. A thermocouple was placed in intimate contact with a small magnesium sample. The sample was heated in an electric furnace at a specified rate in an oxygen atmosphere. The heating curve of the sample shows two distinct branches. A typical curve is shown in Fig. 1. Branch a-b corresponds to the heating of the sample by the furnace and b-c to the heating of the sample by ignition.

From actual observation, it was found that the point b corresponds very nearly to the temperature at which a flame is propagated. Point b then corresponds to the definition of ignition temperature. This definition was adopted because the values of the ignition temperatures are reproducible (i.e.,

Table I. Experimental Vs. Calculated (Eq 4) Ignition Temperatures of Magnesium and Magnesium Alloys

| Alloy       | Oxide Film Thickness, Cm | Calculated °C (Eq 4) | Experimental °C (Authors) |
|-------------|--------------------------|----------------------|---------------------------|
| 1.78 pct Al | $1.35 \times 10^{-2}$    | 551                  | 600*                      |
| 3.81 pct Al | $1.35 \times 10^{-2}$    | 460                  | 582                       |
| Pure Mg     | $5 \times 10^{-2}$       | 642                  | 623                       |
| Pure Mg     | $1 \times 10^{-1}$       | 618                  | 623                       |
| Pure Mg     | $2 \times 10^{-1}$       | 595                  | 623                       |
| Pure Mg     | $5 \times 10^{-2}$       |                      | 623                       |

\* Leontis and Rhines<sup>1</sup> obtained a value of 548°C.

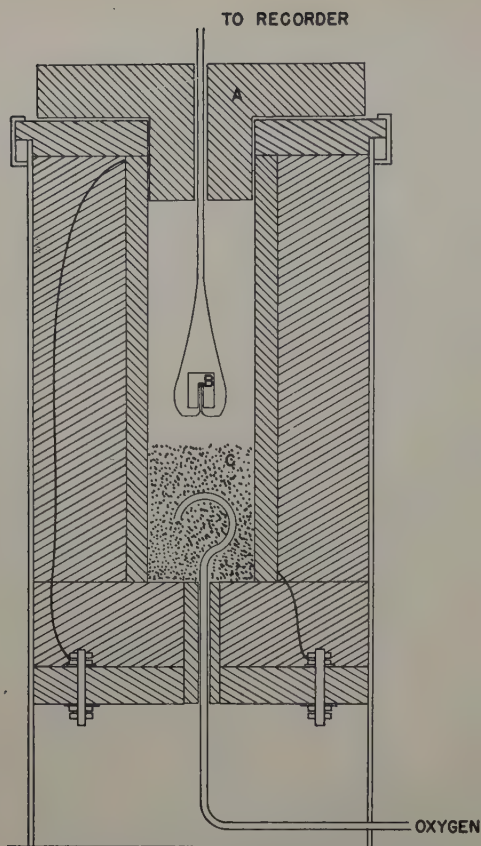


Fig. 2—Furnace used in ignition temperature experiments.

$\pm 5^{\circ}\text{C}$ ) on any given alloy composition. In addition, the ignition temperature is not influenced by complicating factors such as the Constable effect<sup>11</sup> ("self heating" of the sample); size of sample, within reasonable limits; rate of flow of oxygen; time of exposure; and rate of heating.

#### Measurement of Ignition Temperature

The alloy samples were melted in a small induction furnace, cast in a preheated split steel mold ( $\frac{1}{2}$  in. diam  $\times$  3 in.) and turned on a lathe to 0.375 in. and cut into  $\frac{1}{2}$  in. lengths. Power cross feeds of 0.0018 in. per revolution were used to insure uniform surface conditions on all samples. A hole was drilled coaxially  $\frac{3}{8}$  in. deep with a No. 47 wire gage drill to provide a well for the thermocouple.

The hot junction of the thermocouple was inserted into the well of the alloy sample to be tested and the lead wires doubled back to form a U-shaped cradle so that only the junction was in contact with the sample.

Throughout the investigation the ignition temperatures were determined by measuring the temperature of the sample with a chromel-alumel thermocouple (28 gage) connected to a Leeds and Northrop Micromax recorder.

The schematic arrangement of the furnace (Hoskins Type FA120) with the sample in position is shown in Fig. 2. This equipment was used in all ignition temperature determinations in oxygen, oxygen-nitrogen, and oxygen-sulphur dioxide mixtures at atmospheric pressure.

With the sample in position, the flow of pure oxygen or oxygen mixture was started through the bottom of the furnace and adjusted to a rate of 250 ml per min. (The ignition temperature of pure

magnesium was found to remain constant at flow rates from 50 to 500 ml per min.)

After 5 min the furnace was turned on (voltage to furnace held constant at 100 v, i.e. 83 pct rated voltage). Heating was continued until the recorder showed a sharp increase in rate of temperature rise, indicating ignition. After completion of the test, the tangential intersection of the two branches of the heating curve was plotted and the temperature of ignition evaluated.

Oxygen was used for the majority of the ignition temperature determinations. While this does not duplicate the conditions during heat treatment, it does provide comparative results between magnesium and its alloys. When air was substituted for oxygen, somewhat erratic temperatures were obtained, but with oxygen no such difficulty occurred and usually the mean variation did not exceed  $2^{\circ}\text{C}$ .

The ignition temperatures of the following systems have been determined: Mg, Mg-Ag, Mg-Bi, Mg-Co, Mg-Ca, Mg-Ni, Mg-Sb, Mg-Pb, Mg-Zn. In addition a number of other binary alloys have been studied in certain regions as well as a number of

Table II. Ignition Temperatures of Magnesium and Magnesium Alloys in Oxygen at Atmospheric Pressure

| Compo-<br>sition,<br>Pct<br>Alloy-<br>ing<br>Element | Igni-<br>tion<br>Tem-<br>pera-<br>ture,<br>$^{\circ}\text{C}$ | Compo-<br>sition,<br>Pct<br>Alloy-<br>ing<br>Element | Igni-<br>tion<br>Tem-<br>pera-<br>ture,<br>$^{\circ}\text{C}$ | Compo-<br>sition,<br>Pct<br>Alloy-<br>ing<br>Element | Igni-<br>tion<br>Tem-<br>pera-<br>ture,<br>$^{\circ}\text{C}$ |
|------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------------|---------------------------------------------------------------|
| Pure EMCO Mg                                         | 623                                                           | Mg-Ca                                                |                                                               | Mg-Zn                                                |                                                               |
|                                                      |                                                               | 1.0                                                  | 624                                                           | 19.07                                                | 523                                                           |
|                                                      |                                                               | 2.0                                                  | 630                                                           | 19.33                                                | 530                                                           |
| Mg-Al                                                |                                                               | 5.0                                                  | 633                                                           | 19.91                                                | 552                                                           |
| 5.67                                                 | 558                                                           |                                                      |                                                               | 30.14                                                | 513                                                           |
| 5.88                                                 | 527                                                           | Mg-In                                                |                                                               | 30.2                                                 | 534                                                           |
| 11.43                                                | 530                                                           | 10.0                                                 | 613                                                           | 31.74                                                | 524                                                           |
| 13.97                                                | 535                                                           | 20.0                                                 | 593                                                           | 33.48                                                | 524                                                           |
| 18.17                                                | 502                                                           | 30.0                                                 | 586                                                           | 51.13                                                | 568                                                           |
| 26.04                                                | 514                                                           |                                                      |                                                               | 60.72                                                | 542                                                           |
| 33.25                                                | 515                                                           | Mg-Li                                                |                                                               | 69.73                                                | 535                                                           |
| 38.65                                                | 560                                                           | 0.3                                                  | 553                                                           | 76.9                                                 | 541                                                           |
| 53.7                                                 | 535                                                           | 0.8                                                  | 578                                                           | 89.33                                                | 538                                                           |
| 63.15                                                | 462                                                           | 4.0                                                  | 513                                                           |                                                      |                                                               |
| 80.33                                                | None                                                          | 8.0                                                  | 514                                                           | Mg-Al-Zn                                             |                                                               |
| 82.72                                                | to                                                            | 11.4                                                 | 518                                                           | 1.21 Al                                              | 610                                                           |
| 93.73                                                | 900                                                           |                                                      |                                                               | 1.12 Zn                                              |                                                               |
|                                                      |                                                               | Mg-Mn                                                |                                                               | 2.16 Al                                              | 585                                                           |
| Mg-Ag                                                |                                                               | 1.0                                                  | 621                                                           | 2.07 Zn                                              |                                                               |
| 4.8                                                  | 550                                                           | 2.0                                                  | 616                                                           |                                                      |                                                               |
| 9.04                                                 | 537                                                           | 3.0                                                  | 631                                                           | 3.14 Al                                              | 575                                                           |
| 14.12                                                | 540                                                           |                                                      |                                                               | 3.27 Zn                                              |                                                               |
|                                                      |                                                               | Mg-Ni                                                |                                                               | 4.23 Al                                              | 544                                                           |
| Mg-Bi                                                |                                                               | 5.0                                                  | 510                                                           | 4.19 Zn                                              |                                                               |
| 10.0                                                 | 500                                                           | 10.0                                                 | 517                                                           |                                                      |                                                               |
| 20.0                                                 | 548                                                           | 20.0                                                 | 508                                                           | 3.18 Al                                              | 576                                                           |
|                                                      |                                                               |                                                      |                                                               | 4.98 Zn                                              |                                                               |
| Mg-Cd                                                |                                                               | Mg-Sb                                                |                                                               | 5.95 Al                                              | 560                                                           |
| 7.15                                                 | 612                                                           | 1.20                                                 | 582                                                           | 3.58 Zn                                              |                                                               |
| 8.35                                                 | 597                                                           | 4.38                                                 | 585                                                           |                                                      |                                                               |
| 10.78                                                | 588                                                           | 5.22                                                 | 588                                                           | 6.10 Al                                              | 543                                                           |
| 12.54                                                | 593                                                           | 9.0                                                  | 588                                                           | 6.02 Zn                                              |                                                               |
| 14.07                                                | 595                                                           | 21.6                                                 | 593                                                           |                                                      |                                                               |
| 15.75                                                | 603                                                           | 29.1                                                 | 586                                                           | 10.69 Al                                             | 549                                                           |
| 17.86                                                | 587                                                           |                                                      |                                                               | 14.26 Zn                                             |                                                               |
| 20.98                                                | 596                                                           | Mg-Si                                                |                                                               |                                                      |                                                               |
| 23.05                                                | 587                                                           | 1.83                                                 | 610                                                           |                                                      |                                                               |
| 25.31                                                | 607                                                           | 3.15                                                 | 625                                                           |                                                      |                                                               |
| 30.71                                                | 584                                                           |                                                      |                                                               | Mg-Al-Cd                                             |                                                               |
| 33.19                                                | 578                                                           | Mg-Sn                                                |                                                               | 14.75 Al                                             | 534                                                           |
| 35.10                                                | 586                                                           | 9.88                                                 | 576                                                           | 11.26 Cd                                             |                                                               |
| 41.17                                                | 571                                                           | 10.52                                                | 560                                                           |                                                      |                                                               |
| 44.09                                                | 559                                                           | 11.34                                                | 556                                                           | 9.5 Al                                               | 544                                                           |
| 50.93                                                | 541                                                           | 20.33                                                | 571                                                           | 4.98 Cd                                              |                                                               |
| 61.40                                                | 517                                                           | 22.31                                                | 574                                                           |                                                      |                                                               |
| 62.30                                                | 522                                                           | 25.62                                                | 574                                                           |                                                      |                                                               |
| 71.80                                                | 535                                                           |                                                      |                                                               | Mg-Cd-Ag                                             |                                                               |
| 80.73                                                | 533                                                           | Mg-Pb                                                |                                                               | 22.9 Cd                                              | 570                                                           |
| 90.52                                                | 551                                                           | 16.24                                                | 575                                                           | 0.33 Ag                                              |                                                               |
|                                                      |                                                               | 29.97                                                | 565                                                           |                                                      |                                                               |
| Mg-Co                                                |                                                               | 45.98                                                | 553                                                           | 15.3 Cd                                              | 560                                                           |
| 1.0                                                  | 617                                                           | 58.26                                                | 504                                                           | 1.77 Ag                                              |                                                               |
| 5.0                                                  | 616                                                           |                                                      |                                                               | 24.9 Cd                                              | 592                                                           |
|                                                      |                                                               |                                                      |                                                               | 2.22 Ag                                              |                                                               |
| Mg-Cu                                                |                                                               | Mg-Zn                                                |                                                               | 26.77 Cd                                             | 567                                                           |
| 10.3                                                 | 537                                                           | 3.04                                                 | 595                                                           | 2.3 Ag                                               |                                                               |
| 20.5                                                 | 519                                                           | 4.81                                                 | 552                                                           |                                                      |                                                               |
| 30.76                                                | 532                                                           | 5.23                                                 | 546                                                           | Mg-Cd-Zn                                             |                                                               |
|                                                      |                                                               | 9.25                                                 | 509                                                           | 19.9 Cd                                              | 553                                                           |
|                                                      |                                                               | 10.34                                                | 537                                                           | 2.78 Zn                                              |                                                               |
|                                                      |                                                               | 12.5                                                 | 558                                                           |                                                      |                                                               |



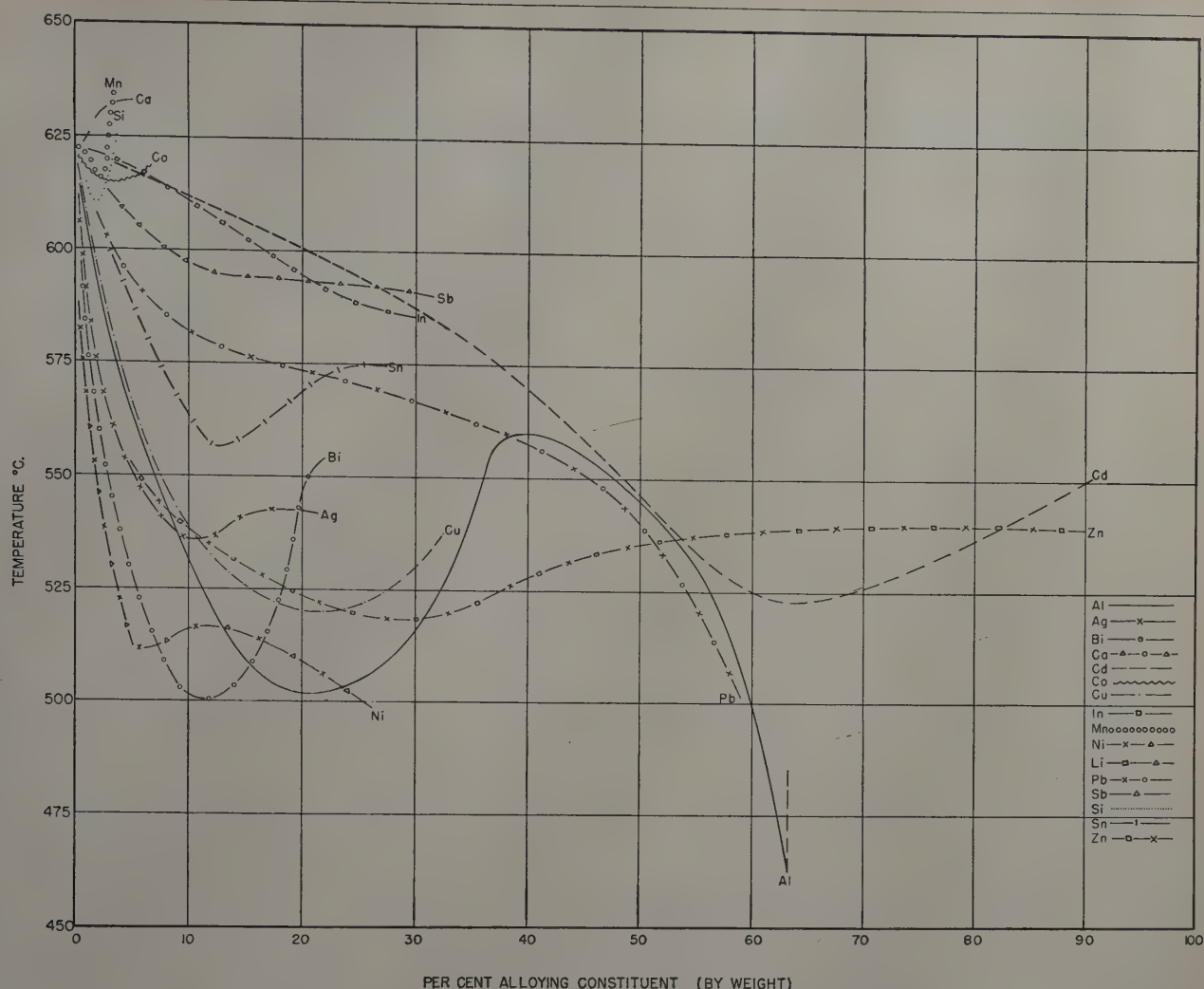


Fig. 3—Effect of alloying elements on the ignition temperature of magnesium.

ternary and quaternary alloys of specific compositions. The results are shown in Table II and summarized in Fig. 3.

The results obtained for magnesium in oxygen-nitrogen mixtures are shown in Table III. The ig-

Table III. Ignition Temperatures of Magnesium in Oxygen-Nitrogen Mixtures

| O, Pct | N, Pct | Ignition Temperature, °C |
|--------|--------|--------------------------|
| 89.5   | 10.5   | 649 629 629              |
| 80     | 20     | 635 632                  |
| 70     | 30     | 641 638                  |
| 60     | 40     | 627 629                  |
| 50     | 50     | 632 632                  |
| 40     | 60     | 627 627 604              |
| 30     | 70     | 627 627                  |
| 20     | 80     | 638 613 624 635          |
| 10     | 90     | 638 635 616              |

Table IV. Ignition Temperatures of Magnesium in Oxygen-Sulphur Dioxide Mixtures

| O, Pct | SO <sub>2</sub> , Pct | Ignition Temperature, °C |
|--------|-----------------------|--------------------------|
| 100    | 0                     | 623                      |
| 99.5   | 0.5                   | 630                      |
| 99.25  | 0.75                  | 638                      |
| 99.0   | 1.0                   | 646                      |
| 97.0   | 3.0                   | 648                      |
| 96.0   | 4.0                   | 649                      |
| 94.2   | 5.8                   | 648                      |

nition temperatures of magnesium in mixtures of oxygen and sulphur dioxide are given in Table IV.

### Delayed Ignition of Magnesium Below Normal Ignition Temperature

As pointed out above, the theory of ignition of magnesium as proposed by Eyring and Zwolinski<sup>9</sup> indicates that the ignition temperature is dependent upon the thickness of the oxide film on the sample. The following series of experiments were conducted to determine the validity of this theory.

**Experimental Procedure:** Preliminary experiments on the ignition of magnesium with prolonged heating showed that the Constable effect<sup>11</sup> (a spontaneous rise in temperature as a result of heat evolved by the oxidation process) may occur at temperatures considerably below the ignition temperature. Due to this spontaneous rise in tempera-

Table V. Time Necessary for Magnesium to "Self Heat" to the Temperature of Ignition

| Sample Number | Constant Furnace Temperature, °C | Sample Temperature at Which Ignition Occurred | Time Interval to Ignition Temperature, Min |
|---------------|----------------------------------|-----------------------------------------------|--------------------------------------------|
| 1             | 623                              | 623                                           | 0.00                                       |
| 2             | 602                              | 623                                           | 34' 26"                                    |
| 3             | 587                              | 623                                           | 213'                                       |

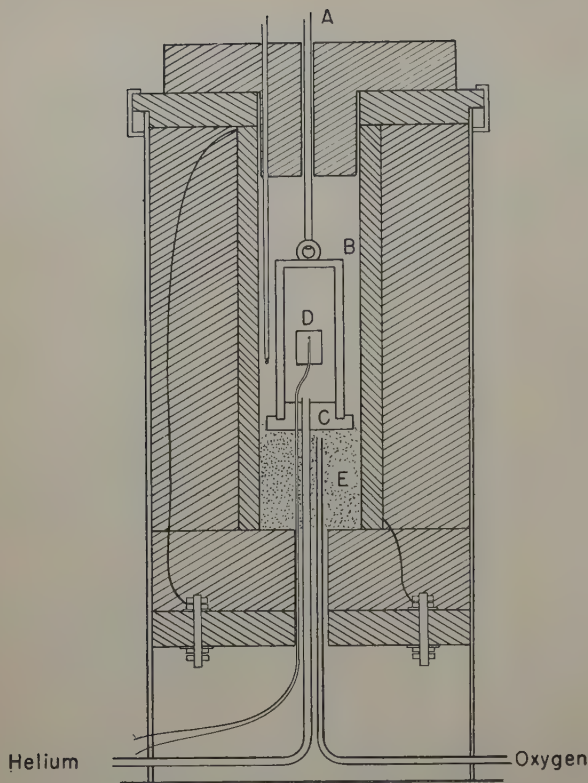


Fig. 4—Furnace and bell used in time delay experiments.

ture, it is necessary to control the temperature of the furnace or bath by a thermocouple in the furnace wall or very near to it. Also, the sample temperature must be measured by a separate thermocouple, since its temperature will be above the furnace temperature at any finite time after the introduction of oxygen.

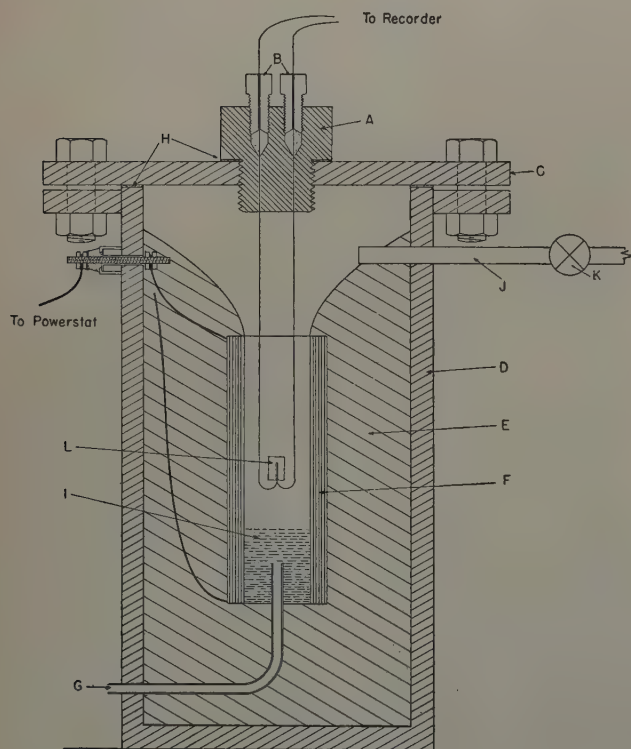


Fig. 5—Pressure ignition furnace.

The equipment used to conduct these experiments was designed to avoid the possible difficulties from the Constable effect. The apparatus is shown schematically in Fig. 4.

The furnace was a Hoskins Type FA 120, the same type as used in the standard ignition determination. The furnace temperature was controlled by means of a thermocouple placed very near the furnace wall and connected to a Leeds and Northrop Micromax temperature controller. The bottom section of the heating chamber was filled with Ottawa sand, *E*, to allow the incoming gases to reach the furnace temperature. A small circular base plate of stainless steel, *C*, was fitted with the sample thermocouple and the sample, *D*, and made so that the bell, *B*, was placed in the sealing ring of the base plate completely covering the magnesium sample. While the furnace was cold, the helium\* flow into the interior of the bell was started to prevent oxidation and continued until temperature equilibrium between the sample and the furnace walls was reached. At the same time oxygen was passed into the heating chamber. When equilibrium was established, the flow of helium was stopped and the bell raised to allow the oxygen to come in contact with the magnesium sample. Time was counted from this instant. When ignition occurred the elapsed time interval was recorded. The results of these experiments are shown in Table V.

#### Change in Ignition Temperature of Magnesium as a Function of Oxygen Pressure

The object of these experiments was to determine if the ignition temperature is a function of oxygen pressure. These data may indicate the type of reaction involved in ignition of the magnesium sample.

**Experimental Procedure:** The procedure for determining the ignition temperature using the special pressure furnace, Fig. 5, is as follows: The thermocouple wires were led through the threaded steel plug, *A*, and the packing glands, *B*. The packing, moistened asbestos fiber, was placed in the conical wells in plug, *A*, and the gland nuts, *B*, screwed into place. The sample, *L*, was suspended by the thermocouple wires and the assembly screwed into the furnace top, *C*, sufficiently tight to seal, *A* and *C*, by means of the lead gasket, *H*. Oxygen was then admitted through the inlet tube, *G*, from the oxygen cylinder via a reduction valve which reduced the pressure to a maximum of 200 psi.

The oxygen passed through the Ottawa sand zone, *I*, and the sample chamber, *B*, of the electrically heated furnace, *F*. The valve, *K*, on the outlet pipe, *J*, was opened and closed intermittently until all air was purged from the system. Valve *K* then was closed and the pressure adjusted to the desired value. The thermocouple wires were connected directly to a Brown recording potentiometer. Heating was then started following the same program as for the standard ignition determination.

The data obtained in the study of the effect of oxygen pressure on the ignition temperature of magnesium is shown in Table VI and Fig. 6.

#### Lowering Ignition Temperature of Magnesium

The lowering of the ignition temperature of magnesium by contact with other metals has not been investigated thoroughly. Preliminary experiments

\* Helium, special purity (no dew point). Furnished through the courtesy of S. R. Zimmerley, U. S. Bureau of Mines, Salt Lake City.



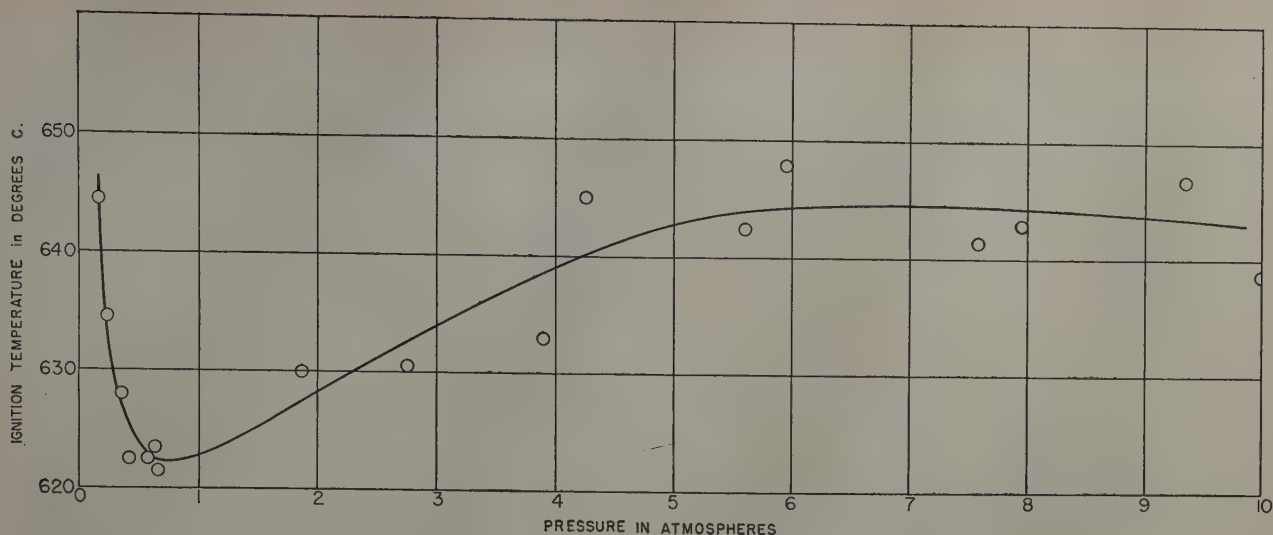


Fig. 6—Ignition temperature of magnesium with respect to oxygen pressure.

performed in this laboratory indicate that the ignition temperature of magnesium is lowered appreciably by contact with aluminum, nickel, and 70-30 brass. Silver and plain carbon steel did not affect the ignition temperature. The samples were prepared by drilling a hole through a piece of pure magnesium followed by reaming with a 2/0 taper pin reamer. The dissimilar metal in the form of a pin was driven in and the ends turned off thus giving a perfect contact. The values of the ignition temperatures of pure magnesium in contact with other metals are presented in Table VII (oxygen atmosphere).

#### Discussion of Results

The method developed for the determination of the ignition temperatures of magnesium and magnesium alloys is simple and reproducible. As an illustration of the accuracy of this test, ten samples of magnesium of the same lot were run in oxygen by four different individuals over a period of six months. The average ignition temperature obtained from this series of tests was:

$$623^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$$

The ignition temperature of magnesium generally is lowered by the addition of alloying elements providing the melting point (liquidus) is lower than pure magnesium. Ignition of magnesium alloys may occur at temperatures either above or below the

Table VI. The Ignition Temperature of Magnesium in Oxygen as a Function of Pressure

| Oxygen Pressure, Atm | Ignition Temperature, °C | Average Ignition Temperature |
|----------------------|--------------------------|------------------------------|
| 0.166                | 643 645                  | 644.5                        |
| 0.234                | 636 633                  | 634.5                        |
| 0.365                | 628 628                  | 628                          |
| 0.42                 | 622 623                  | 622.5                        |
| 0.58                 | 623 622                  | 622.5                        |
| 0.64                 | 623 624                  | 623.5                        |
| 0.688                | 621 622                  | 621.5                        |
| 1.0                  | 623                      | 623                          |
| 1.865                | 630 630 629 631          | 630                          |
| 2.75                 | 633 628                  | 630.5                        |
| 3.9                  | 635 631                  | 633                          |
| 4.25                 | 645 645                  | 645                          |
| 5.6                  | 644 641                  | 642.5                        |
| 5.95                 | 649 647                  | 648                          |
| 7.68                 | 641 642                  | 641.5                        |
| 7.95                 | 641 644 644              | 643                          |
| 9.35                 | 647 647                  | 647                          |
| 10.0                 | 640 638 638              | 638.8                        |

melting point indicating that the conclusions of Carapella and Shaw<sup>8</sup> are not generally valid. The Mg-Cd system, Fig. 3, is an excellent example of this effect. The melting point of the alloy has some influence on the ignition temperature, but it is not the only factor that must be considered. This is discussed in detail in ref. 14.

One rather unusual observation was made of the magnesium and magnesium alloy samples just prior to ignition. Normally the oxide coating present is white in color. However, just an instant before ignition occurs, the oxide coating turns a dark brown or black color. Once the color change occurs, ignition follows immediately.

A correlation exists between the rates of linear oxidation and the ignition temperatures of magnesium alloys. Sufficient data to justify its presentation is available only on the Mg-Al system. Qualitatively, however, all of the alloy compositions investigated by Leontis and Rhines show the same relationship. Table VIII shows the correlation of the linear oxidation rates and the ignition temperatures of some Mg-Al alloys.

The ignition temperature of magnesium in oxygen-sulphur dioxide mixtures increases from 623°C at zero percent SO<sub>2</sub> to approximately the melting point of magnesium (650°C) at 1.7 pct SO<sub>2</sub>. From 1 to 5.8 pct SO<sub>2</sub> no further increase is observed. Qualitatively, at least, it is well known that high concentrations of SO<sub>2</sub> prevent the ignition of magnesium at temperatures considerably above the melting point. Thus, a further increase in the ignition temperature would be expected at concentrations above 5.8 pct SO<sub>2</sub> which was the maximum concentration investigated in this work.

The results obtained on the time-delay of the ignition of magnesium show that if the furnace or bath

Table VII. Ignition Temperatures of Magnesium in Contact with Other Metals

| Sample | Contact Metal | Ignition Temperature, °C |
|--------|---------------|--------------------------|
| Mg     |               | 623                      |
| Mg     | Ni            | 588                      |
| Mg     | Ag            | 623                      |
| Mg     | 70-30 brass   | 538                      |
| Mg     | Steel         | 623                      |
| Mg     | Al            | 523                      |

Table VIII. The Relation of the Ignition Temperature to the Oxidation Rate of Mg-Al Alloys

| Alloy,<br>Pct by Wt | Oxidation Rate,*<br>Mg per Sq Cm<br>per Hr 475°C | Ignition<br>Temperature,<br>°C |
|---------------------|--------------------------------------------------|--------------------------------|
| Mg                  | 0.01                                             | 623                            |
| Mg-1.78% Al         | 0.025                                            | 605                            |
| Mg-3.18% Al         | 0.051                                            | 580                            |
| Mg-7.23% Al         | 0.305                                            | 558                            |
| Mg-9.12% Al         | 7.7†                                             | 543                            |
| Mg-18.66% Al        | 17.0†                                            | 503                            |

\* Sources, ref. 1.  
† Extrapolated.

is maintained at some constant temperature below the ignition temperature of magnesium in oxygen, the magnesium will autoheat to the ignition temperature. The ignition temperature obtained under the conditions imposed in the time-delay experiments is identical with the value obtained in the normal ignition temperature experiments.

The approximate thickness of the oxide films present on the samples listed in Table V may be calculated from the oxidation rate data of Leontis and Rhines and an approximate value for the density of the MgO film as 0.8 g per cc. The approximate thicknesses are: Sample 1, Table V,  $5 \times 10^{-7}$  cm; Sample 2,  $1.56 \times 10^{-3}$ ; Sample 3,  $5.5 \times 10^{-3}$ . Thus the oxide film thickness changes by a factor of  $10^4$  cm yet the ignition temperature remains unchanged. This is not in agreement with the predicted results of Eyring and Zwolinsky,<sup>10</sup> see Table I.

The results obtained on the change of ignition temperature of magnesium with respect to oxygen pressure conclusively prove that the ignition reaction of magnesium is oxygen pressure dependent. The ignition temperature of magnesium increases with an increase in total oxygen pressure from 1 to 10 atm pressure. Below atmospheric pressure, the ignition temperature decreases with a minimum at about 0.4 atm, rising again at lower pressures.

The theory of ignition of metals and alloys by Eyring and Zwolinski does not account for the effect of oxygen pressure on the ignition temperature. If eq 2 is used, adsorption on the activated sites is assumed. Under increased pressures the velocity of the reaction should increase causing a decrease in the ignition temperature. This, of course, is in direct contradiction to the experimental results of the authors on ignition and of the work of Leontis and Rhines<sup>1</sup> and E. A. Gulbransen<sup>15</sup> on oxidation of magnesium.

Dissimilar metal contacts generally lower the ignition temperature of magnesium by localized diffusion and alloy formation. This would cause a small zone in which the rate of reaction is increased, accompanied by a lowering of the ignition temperature. This result has also been obtained by Willmore and Peterson.<sup>8</sup>

## Summary

A simple reproducible method of determining the ignition temperature of magnesium and magnesium alloys has been developed. This method was used to determine the ignition temperature of over 100 different magnesium alloys in oxygen at atmospheric pressure. The ignition temperature of pure magnesium was investigated in oxygen-nitrogen, oxygen-sulphur dioxide, and in oxygen from 0.166 to 10.0 atm pressure. The ignition temperature of magnesium generally is lowered by the addition of alloying elements. Ignition of magnesium alloys may occur either above or below the liquidus line. The ignition reaction of magnesium is pressure dependent, and hence any theory of ignition must satisfy this fact.

## Acknowledgments

The authors wish to express their thanks to the Technical Command, Army Chemical Corps, whose sponsorship made this work possible. The authors also wish to express their gratitude for assistance given by M. A. Cook, Professor of Metallurgy, University of Utah, and by J. Blackledge, D. Richins and LeRoy Jackman, Graduate Students at the University of Utah.

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## Correction

In the March 1951 issue: *Solubility of Hydrogen in Molten Lead* by W. R. Opie and N. J. Grant. P. 245, the second equation should read:

$$\text{Log}_{10}K = \frac{-\Delta H}{4.575 T} + C$$



# Rate of Sintering of Copper Under a Dead Load

by F. N. Rhines and H. S. Cannon

The application of a static load to a copper powder compact during sintering at an elevated temperature accelerates the rate of sintering in such a way that a given load induces the same proportional increase in rate for all times of sintering. It is shown that sintering under a load is like creep under a fixed load in that the stress required to accomplish a given degree of densification is proportional to the logarithm of the sintering time.

VIRTUALLY all of the theories of sintering that have been put forward within recent years have contained the assumption that the chief driving force of the process is the surface tension resident in the exposed surfaces and internal pores of the compact, or powder mass. An externally applied load might be expected to provide a somewhat equivalent driving force for sintering. It is known that the application of a compressive load, during sintering, hastens densification, but it is by no means clear whether sintering under the influence of surface tension alone and sintering under an applied load are fundamentally similar processes. The present study was undertaken in an effort to obtain an answer to this question and with the hope that the answer may contribute to an understanding of the mechanism of sintering. It has been found that there is a close relationship between sintering and creep processes.

Copper powder compacts were sintered in hydrogen at 1000°C under dead loads of 0 to 165 psi and the progress of sintering was observed by means of density measurements. Using a commercial reduced oxide copper powder, see Table I, cylindrical compacts ½ in. x ½ in. high were made at a pressure of 12,500 psi. For sintering, these were placed in a cylindrical graphite container into which they fitted snugly. A compressive axial load was applied to the compact through a graphite rod of similar diameter, which rested upon the upper end face of the compact; iron weights, in suitable amount, were placed upon the graphite rod to provide the load. This assembly was encased in a vertical silica tube

Table I—Analysis of Copper Powder

| Mesh Number           | Percentage |
|-----------------------|------------|
| +150                  | 0.1        |
| +200                  | 13.0       |
| +250                  | 4.6        |
| +325                  | 13.4       |
| —325                  | 68.9       |
| Hydrogen loss, pct    | 0.19       |
| Apparent density      | 2.47       |
| Flow rate, sec        | 30.4       |
| Fisher sub-sieve size | 7.8        |

Table II—Density of Compacts Sintered under Load\*

| Load, Psi | Time, Hr | Density | Ideal Density, Pct |
|-----------|----------|---------|--------------------|
| 0         | 0        | 4.75    | 54.3               |
| 0         | 1        | 7.05    | 78.7               |
| 0         | 3        | 7.61    | 85.0               |
| 0         | 10       | 8.16    | 91.0               |
| 0         | 96       | 8.73    | 97.4               |
| 10.5      | 1        | 7.35    | 82.0               |
| 10.5      | 7        | 8.13    | 90.7               |
| 10.5      | 110      | 8.78    | 98.0               |
| 30        | 1        | 7.57    | 84.5               |
| 30        | 10       | 8.42    | 94.0               |
| 30        | 100      | 8.80    | 98.2               |
| 70.5      | 1        | 8.21    | 91.6               |
| 70.5      | 3        | 8.44    | 94.2               |
| 70.5      | 11       | 8.69    | 97.0               |
| 70.5      | 34       | 8.78    | 98.0               |
| 70.5      | 98       | 8.87    | 99.0               |
| 125       | 1        | 8.53    | 95.2               |
| 165       | 1        | 8.64    | 96.4               |

\* Compacts prepressed at 12,500 psi. All sintering conducted at 1000°C in hydrogen.

within a resistance-type furnace capable of maintaining a substantially constant temperature within the working zone. After various predetermined times at temperature, the samples were removed from the furnace and their density was measured by conventional means. The heating-up and cooling-down times have been included in the computed sintering time, using the assumption that the sintering rate doubles for each increase of 10°C in temperature. The experimental results are presented in Table II.

Upon metallographic examination of the specimens, it was found that there was no apparent change in the shape of the pores as a result of loading, i.e. no flattening, Fig. 1. Substantial contraction away from the container walls was observed in all samples sintered with loads of 10.5 psi and less.

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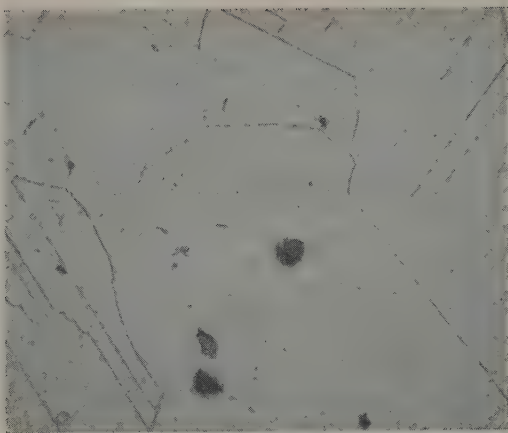


Fig. 1. Typical appearance of pores after 98 hr at 1000°C under a load of 70.5 psi, prepressed sample. X500.

A few experiments were made, also, using a loose powder fill in the graphite container. Again, the sintering temperature was 1000°C and the atmosphere was hydrogen. The results, shown in Table III, are similar to those for the sintering of prepressed powders except that longer times are required to attain a given density value under a given load. It is interesting that loose powder can be sintered to a density as high as 98 pct of the ideal, under a load as small as 115 psi, in as little as five days.

#### Discussion of Results

It is characteristic of sintering that the density approaches its ideal value for massive metal at a continually decreasing rate, so that complete densification is not attained within experimentally feasible times. This is seen to be true, also, when a moderate load is applied. The rate of densification is increased by loading, but within the range of loads here employed, the final approach to the ideal density is very gradual and full densification has not been attained. That sintering progresses under load in the same manner as without load is shown by Graph A, Fig. 2, wherein the "densification parameter",  $\alpha$ , is seen to be independent of time. The "densification parameter" is the ratio of the change in the percentage of porosity due to loading (at fixed time) to the percentage of porosity (at the same time) when no load has been applied:

$$\alpha = \frac{P_t - P_p}{P_t}$$

where:  $P_t$  is the percentage of porosity in an unloaded sample, and  $P_p$  is the percentage of porosity in a loaded sample sintered for the same length of time. Thus, a given load produces a constant proportional increase in densification, independent of time.

This suggests that loading, with low loads at least,

Table III—Density of Loose Powder Sintered under Load\*

| Load, Psi | Time, Hr | Density | Ideal Density, Pct |
|-----------|----------|---------|--------------------|
| 0         | 0        | 2.47    | 27.5               |
| 0         | 76       | 7.93    | 88.5               |
| 0         | 106      | 8.31    | 92.7               |
| 10        | 3        | 6.93    | 77.3               |
| 115       | 120      | 8.81    | 98.3               |

\* All sintered at 1000°C in hydrogen.

does not introduce any new mechanism into the sintering process and that the applied force is merely added to the forces (surface tension) normally present in sintering. This interpretation is fortified by the absence of any change in the shape of the pores, as a result of loading, and by the finding of radial shrinkage in samples in which the sintering rate has been accelerated materially by axial loading.

If this conclusion is justified, it becomes apparent that there is a marked similarity between sintering and creep processes, wherein gradual deformation is induced by moderate loading. It is awkward, because of the different geometrical factors involved, to compare sintering rates with creep rates, as a test of their similarity, but it is feasible to compare the two processes in another way. It is well established that the load required to produce a given deformation in steady state creep is a linear function of the logarithm of time. A similar relationship can be demonstrated for sintering, see Graph B, Fig. 2, if

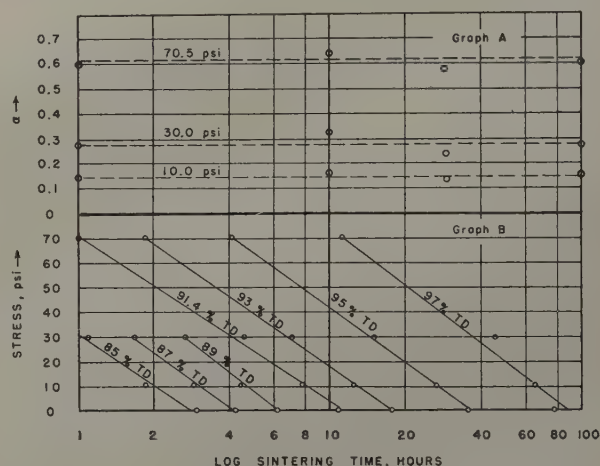


Fig. 2—Densification curves.

the load required to cause densification to progress to a given value is plotted as a function of the logarithm of time. Straight line plots appear justified by the data, and it is to be noted, further, that the point for zero load (ordinary sintering) generally falls upon the line.

In considering these results it should be remembered that the range of loads tested is not large. Were much higher loads used it is to be expected that different results would be obtained, because the creep process itself changes at higher loads, steady state creep giving way to a meeting of the initial and final transient creep mechanisms. At extremely low loads, if it be imagined that the surface tension forces could be taken away, or neutralized, it should be expected again that the process would change, for there appears to be a lower limit to the force that will induce observable creep. It is suggested, therefore, that the plots of Graph B are probably the intermediate straight segments of S-curves which should terminate at infinite time at zero load and at some load lower than the extrapolated values of the present curves at zero time.

Relating sintering and creep in this way does not solve the problem of the mechanism of either process. It does suggest, however, that what is learned about the mechanism of one may be applied to the other, thereby increasing the store of knowledge that may be applied to each.



# Observations on Cleavage and Polygonization Of Molybdenum Single Crystals

by

Neng-Kuan Chen  
and  
Robert Maddin

THE {001} planes have been reported as the cleavage planes in body-centered cubic metals such as alpha-iron and tungsten.<sup>1</sup> However, in molybdenum, which is also body-centered cubic, experimental X-ray evidence indicating a similar cleavage plane still seems lacking. Tsien and Chow<sup>2</sup> observed microscopically in the extension at around 1000°C of molybdenum single crystalline wires 0.25 mm in diam that the fracture plane seemed to be

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parallel to the operative slip plane, which appeared to be {110} at that temperature. Zapffe<sup>3</sup> pointed out from fractographic study of polycrystalline molybdenum that "although the transgranular pattern is characteristically non-crystallographic, patterns occasionally reveal {100} cleavage." This has been generally assumed to be the case at ordinary temperatures.

In the present experiments, a single crystal of Fansteel molybdenum,  $\frac{1}{8}$  in. diam x 2 in. long, prepared by the methods described by Chen, Maddin, and Pond<sup>4</sup> was fractured at room temperature by bending. The fracture surface appeared to be quite similar to the cleavage surface of zinc and was crystallographic. A back-reflection Laue photogram was made using 35 kv copper white radiation; the X-ray

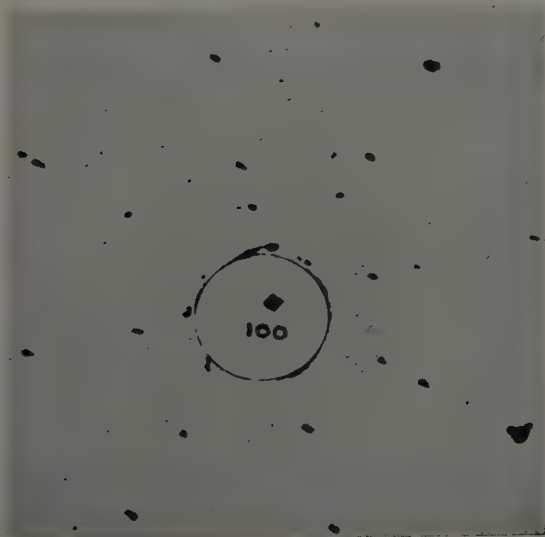


Fig. 1—Laue back-reflection photogram. X-ray beam perpendicular to (100) cleavage face of a molybdenum single crystal.

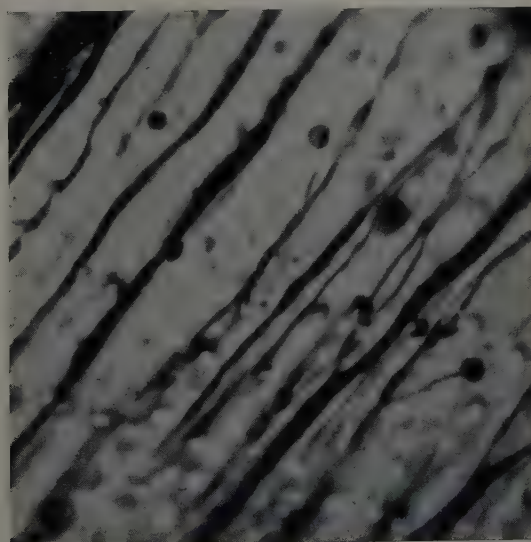


Fig. 2—Slip lines in a molybdenum single crystal at about 2400°C. X800.

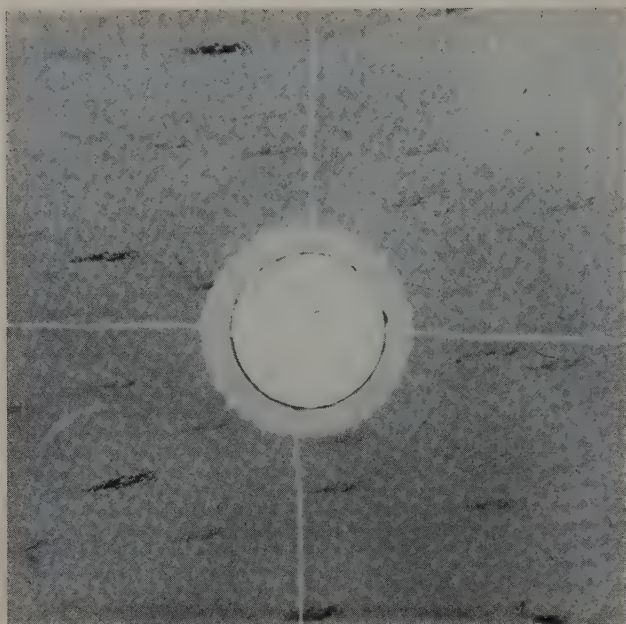
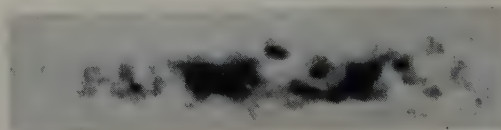


Fig. 3 (left)—Laue back-reflection photograph of a single crystal of molybdenum bent at about 2400°C.

Fig. 4 (below)—Enlargement of a Laue streak shown in Fig. 3. Streak is  $4\frac{1}{2}^\circ$  long.



beam was perpendicular to the cleavage surface. From Fig. 1 it can be concluded that the (100) plane is the plane of cleavage.

An interesting phenomenon apart from the cleavage described above was the polygonization of a single crystal of molybdenum after being bent at around 2400°C. The specimen was  $\frac{1}{8}$  in. in diam x 6 in. long containing a single crystal in the center section about  $1\frac{1}{4}$  in. long. It was polished electrolytically and then reheated in the modified Andrade furnace<sup>4</sup> to a temperature of about 2400°C in 30 min. The specimen expanded freely up to a temperature of about 2200°C as measured by a dilatometer. At a temperature of between 2300° and 2400°C, the expansion was inhibited in some manner so as to cause a sudden sharp dip in the dilatometer reading. After examination at room temperature, a sharp bend through an angle of 15° was noted in the single crystal.

Slip lines observed at room temperature were broad and well-marked and appeared to be very branched, Fig. 2. X-ray photographs taken on three sides of the bent section revealed the orientation of the original crystal. However, the Laue spots were elongated and divided into small individual areas as shown in Figs. 3 and 4. The break-up of Laue spots in deformed crystals after annealing has been observed in aluminum, sodium, zinc and silicon ferrite. It has been termed polygonization by Orowan and Cahn.<sup>5</sup> They reasoned that an elastically bent lattice could be transformed into strain-free polygons by annealing. Recent work by Dunn and Daniels<sup>6</sup> on silicon-iron crystals also confirmed this phenomenon. Thus the present observation on the polygonization of a bent single crystal of molybdenum at high temperature is comparable to the behavior of other metals.

A stereographic plot of the Laue streaks in Fig. 3 is shown in Fig. 5. It should be noted that the rotation of the crystallites is about a [112] axis, which is in the slip plane (110) and 90° from the slip direction [111]. This checks with the microscopic observations of slip and also confirms the general type of crystal rotation in the plastic deformation of single crystals.

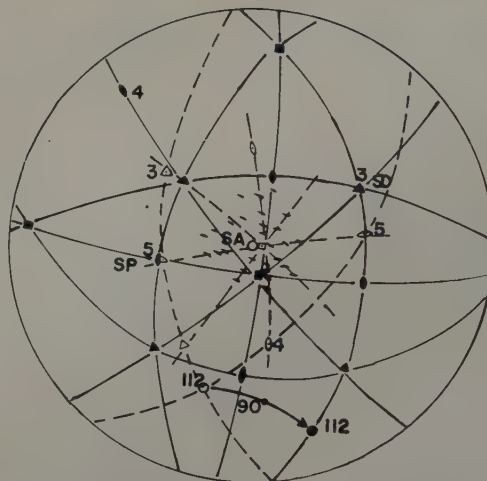


Fig. 5—Stereographic projection of Laue streaks (Fig. 3) showing crystal rotation.

Open representations show the beam perpendicular to the plot at center and stress axis coincides with horizontal diameter. Closed representations show X-ray beam and stress axis perpendicular to plot at center. SD, SP, and SA refer to slip direction, slip plane, and stress axis, respectively.

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# Secondary Recrystallization in Copper Wire

by Guido Bassi

IT is known<sup>1-3</sup> that secondary recrystallization occurs in copper sheet with at least 90 pct reduction after annealing at high temperatures, 700° to 1000°C. Turkalo and Turnbull<sup>4</sup> have found recently that secondary recrystallization might occur even after annealing at such low temperatures as 500°C for a high purity, coarse-grained copper sheet. It will be shown in the following that in an electrolytic tough pitch copper wire, with a high degree of deformation, secondary recrystallization might occur at even lower temperatures.

A hot-rolled rod of 9.5 mm diam (temperature at which rolling commenced was 850°C) was drawn in continuous drawing machines to 0.4 mm, corresponding to a cross-section reduction of 99.8 pct. The texture in the center of the wire (the sample for X-ray analysis was etched to 0.15 mm diam) is a mixture of the [111] and the [100] direction, as

can be seen from Fig. 1. This is in accordance with the result of Schmid and Wassermann.<sup>5</sup> After a few minutes annealing of the wire at 200°C, there is a noticeable recrystallization of the structure with a preferred orientation in the [100] direction at the expense of the [111] deformation texture, as Figs. 2 and 3 show. Farnham and O'Neill<sup>6</sup> reported a similar result. The final recrystallized structure shows mainly the [100] orientation. There is however a small amount of [111] and random orientations.

If the wire is annealed at 400°C, the recrystallized structure first shows a [100] texture, Fig. 4, but as the annealing time is increased the fine-grained structure transforms into coarse grains, Fig. 5, giving a new preferred orientation, Fig. 6. The calculations show this to correspond to the [112] direction. Even if the annealing that gives the primary recrystallization is carried out for six weeks at 200°C, the same secondary recrystallization texture is obtained if the annealing is continued at 400°C. Schmid and Wassermann<sup>7</sup> found the [112] texture, but only after annealing at 1000°C or higher.

The appearance of a secondary recrystallized

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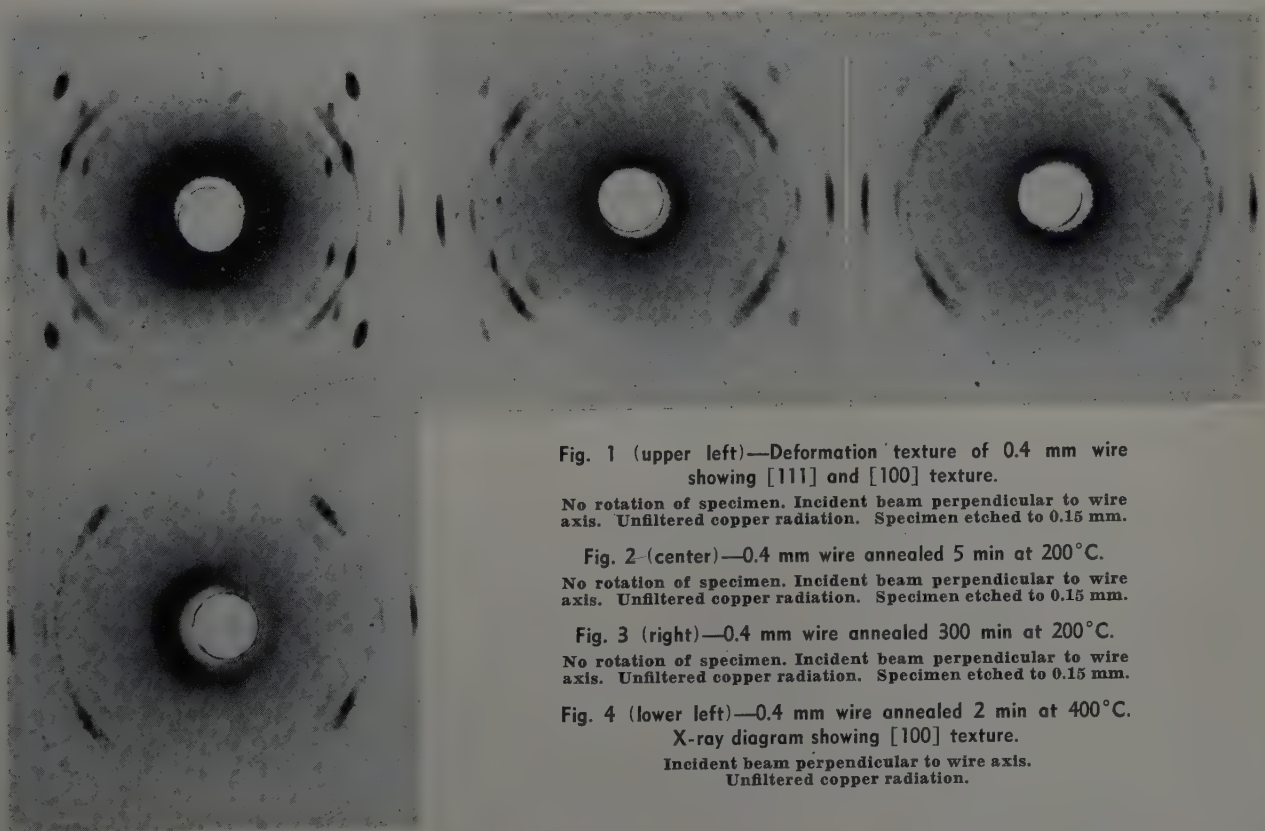


Fig. 1 (upper left)—Deformation texture of 0.4 mm wire showing [111] and [100] texture.

No rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

Fig. 2 (center)—0.4 mm wire annealed 5 min at 200°C.

No rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

Fig. 3 (right)—0.4 mm wire annealed 300 min at 200°C.

No rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

Fig. 4 (lower left)—0.4 mm wire annealed 2 min at 400°C.

X-ray diagram showing [100] texture.  
Incident beam perpendicular to wire axis.  
Unfiltered copper radiation.

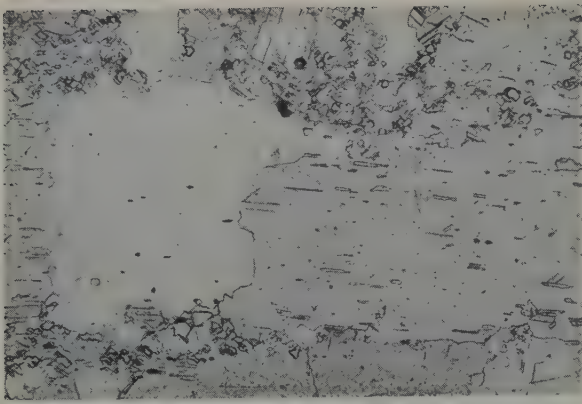


Fig. 5—0.4 mm wire annealed 30 min at 400°C. X200.

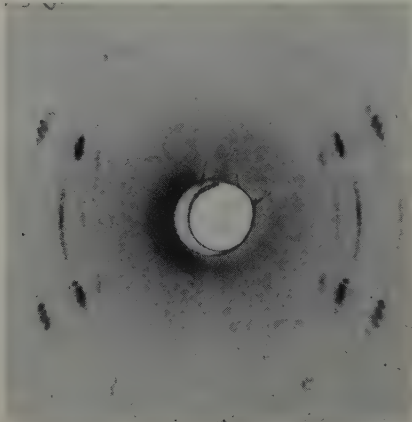


Fig. 6—0.4 mm wire annealed 30 min at 400°C showing [112] texture. Rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

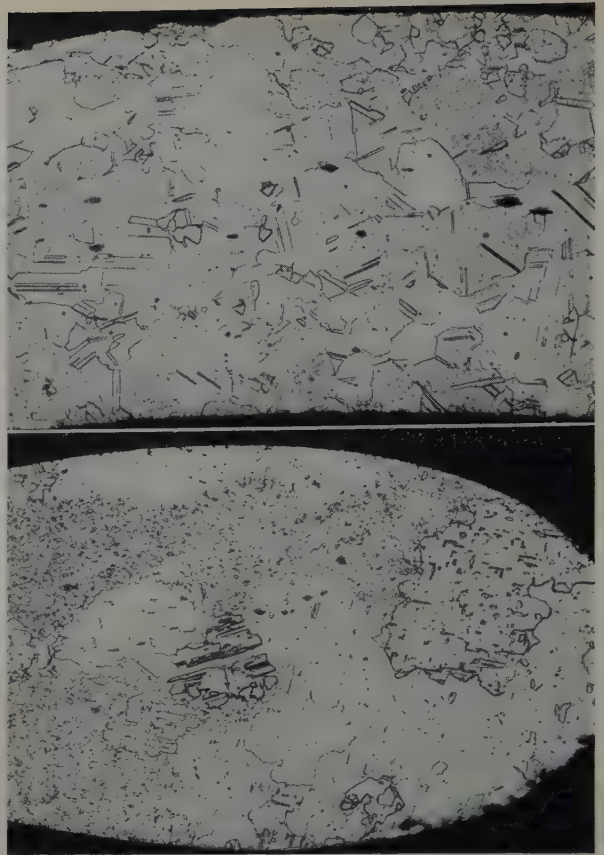


Fig. 7 (top)—9.5 mm hot-rolled rod annealed 1 hr at 1050°C, drawn to 0.4 mm, annealed 320 min at 400°C. X200.

Fig. 8 (bottom)—0.4 mm wire annealed 6 hr at 200°C, drawn to 0.38 mm, annealed 16 hr at 200°C. X200.

structure aligned in the [112] direction at such a low temperature as 400°C is due partly to the very high degree of deformation of the wire. The following two experiments show that the deformation is not the only factor of importance.

1—If electrolytic tough pitch copper is extruded at 925°C into a rod of 19 mm diam (average grain size, 0.05 mm) and drawn to 0.5 mm, corresponding to a reduction of 99.9 pct, then secondary recrystallization is found only after annealing at 800°C or higher. The interference spots on the X-ray film are not so sharp as in Fig. 6.

2—If the earlier mentioned hot-rolled rod of 9.5 mm is annealed 1 hr at 1050°C before being drawn to 0.4 mm, then the final recrystallized structure has a random orientation after annealing at 400°C. The grains are not too coarse, Fig. 7.

The deformation textures from these two experiments were similar to that of Fig. 1 and both showed a primary recrystallization structure with the [100] texture. The observations indicate that the occurrence of secondary recrystallization at 400°C, and the sharpness of the resulting texture are affected by other factors of the previous treatment, in addition to the final deformation. This may be the second last deformation and annealing. After the second last annealing there are areas or grains that are given a higher energy than the average in the last deformation. After the primary recrystallization these high energy grains have become grains with a lower energy than the average. As the annealing goes on, these grains grow at the expense of the neighboring grains with a higher energy. This theory regards secondary recrystallization merely as a coarsening of the primary recrystallized structure.

The [112] texture can be obtained at still lower temperatures. If the hard-drawn wire of 0.4 mm first is annealed 6 hr at 200°C, giving the [100] texture, and then drawn to 0.38 mm, corresponding to a reduction of 9.5 pct, secondary recrystallization with the [112] texture occurs even at 200°C, Fig. 8. Wilson and Kronberg<sup>3</sup> showed a similar result with coarse grains when giving a light reduction to a copper sheet with the cube texture. They regarded this not as secondary recrystallization but as primary recrystallization after critical deformation. It has not been found before however that primary recrystallization can occur after such a low reduction as 9.5 pct and annealing at 200°C. It seems more logical to call it secondary recrystallization.

### Acknowledgment

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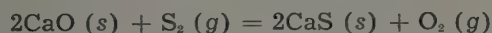
# A Thermodynamic Study of the Reaction $\text{CaS} + \text{H}_2\text{O} \rightleftharpoons \text{CaO} + \text{H}_2\text{S}$ And the Desulphurization of Liquid Metals with Lime

by Terkel Rosenqvist

THE desulphurization of molten iron and steel is a very complicated process. One way to arrive at a better understanding of this process is to break it down into several simpler chemical processes that can be studied individually in the laboratory. For a study of the different factors that influence the equilibrium distribution of sulphur between liquid metals and slags, several simpler equilibria may be investigated. One very important subject is the determination of the escaping tendency of sulphur in the liquid metal and its dependency on temperature and composition of the melt. Several papers in this field have recently been published.<sup>1, 2</sup>

Another subject is the study of the sulphur capacity of the slag. A molten slag is indeed complex, and even if sulphur distribution data for a large variety of molten slags may give empirical data about their desulphurizing power, the importance of the individual components is still not quite clear. It is accepted generally that lime is the most important desulphurizing component in the slag. The present investigation has as its purpose to study the desulphurizing power of lime in its standard state, and to provide a basis for thermodynamic calculations of the desulphurizing power of various lime-containing slags.

The standard state of lime at steelmaking temperatures is solid calcium oxide,  $\text{CaO}$ . It can react with sulphur to form solid calcium sulphide,  $\text{CaS}$ . The relative stability of calcium oxide and calcium sulphide is expressed by the free energy of the reaction:



The existing free energy data for this reaction, listed by Kelley<sup>3</sup> and Osborn,<sup>4</sup> are uncertain to about 10 kcal and are of limited value for a calculation of equilibrium constants.

Under the conditions prevailing in a melting furnace, the sulphur pressure may be expressed conveniently by the ratio  $\text{H}_2\text{S}/\text{H}_2$  and the oxygen pressure by the ratio  $\text{H}_2\text{O}/\text{H}_2$  (or  $\text{CO}_2/\text{CO}$ ). The desulphurizing power of calcium oxide may, therefore, be studied by the reaction  $\text{CaO} + \text{H}_2\text{S} = \text{CaS} + \text{H}_2\text{O}$ .

A study of this reaction may be complicated by certain side reactions: Water vapor and hydrogen sulphide may react to form sulphur dioxide, and calcium sulphide may be oxidized to calcium sulphate. A thermodynamic calculation shows that these side reactions will be suppressed to insignificance if the equilibrium is studied in the presence of an excess of hydrogen.

The apparatus used is shown in Fig. 1. About 10 g calcium oxide and 20 g calcium sulphide (laboratory

qualities) were intimately mixed, and some water was added to make a thick paste. The paste was put into a thimble of zirconium silicate, which was placed within the constant temperature zone of a furnace, and capillary refractory tubes were attached in both ends. After the mixture had been heated in dry hydrogen at  $1000^\circ\text{C}$  for several hours all  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  had decomposed and  $\text{CaSO}_4$  was reduced, so only  $\text{CaO}$  and  $\text{CaS}$  remained in the thimble forming a porous plug.

The mixture was examined by X-ray diffraction after the initial reduction in dry hydrogen as well as after the subsequent experimental runs up to  $1425^\circ\text{C}$ . It was shown that crystalline calcium oxide and calcium sulphide were always present together in about equal amounts. The unit cell edges were found to be 4.80 Å for  $\text{CaO}$  and 5.68 Å for  $\text{CaS}$  in good agreement with existing literature values.<sup>5</sup> This shows that the mutual solid solubility is very small, and that the compounds are present in their standard states.

Purified hydrogen was passed through water saturators kept at constant temperature in a thermostat bath. The amount of water vapor saturation was checked by means of a dew point method, not shown on Fig. 1. The gas mixture was passed through the capillary inlet into the furnace, where it was sifted through the porous plug of calcium oxide and calcium sulphide.

The hydrogen sulphide present in the outgoing gas was absorbed in a zinc acetate solution and the hydrogen was collected over water. When one liter of hydrogen had been collected, the amount of hydrogen sulphide was determined by iodometric titration. As one molecule of  $\text{H}_2\text{O}$  is used for the formation of each molecule of  $\text{H}_2\text{S}$ , the equilibrium

ratio  $\text{H}_2\text{S}/\text{H}_2\text{O}$  would be  $\frac{(\text{H}_2\text{S})}{(\text{H}_2\text{O}) - (\text{H}_2\text{S})}$ , where

$(\text{H}_2\text{O})$  is the molar concentration in the ingoing gas, and  $(\text{H}_2\text{S})$  the molar concentration in the outgoing gas. In the present work  $(\text{H}_2\text{S})$  was always very small compared to  $(\text{H}_2\text{O})$ .

In order for the observed  $\text{H}_2\text{S}/\text{H}_2\text{O}$  ratio to represent the true equilibrium ratio the gas flow has to be: 1—Sufficiently slow to give a complete establishment of equilibrium, and 2—sufficiently fast to counteract thermal diffusion. Incomplete reaction would give a value decreasing with increasing flow rate, and thermal diffusion would give a value increasing with decreasing flow rate. When inlet and outlet tubes of about 2 sq mm cross-section were used, the observed gas ratio was independent of the flow rate between 15 and 125 cc per min, Fig. 2. In this range, therefore, the observed gas ratio represents true equilibrium.\* For the rest of the in-

\* This was not found to be true when the inlet and outlet tubes were of about 20 sq mm cross-section. In that case thermal diffusion was significant at a flow rate of 125 cc per min.

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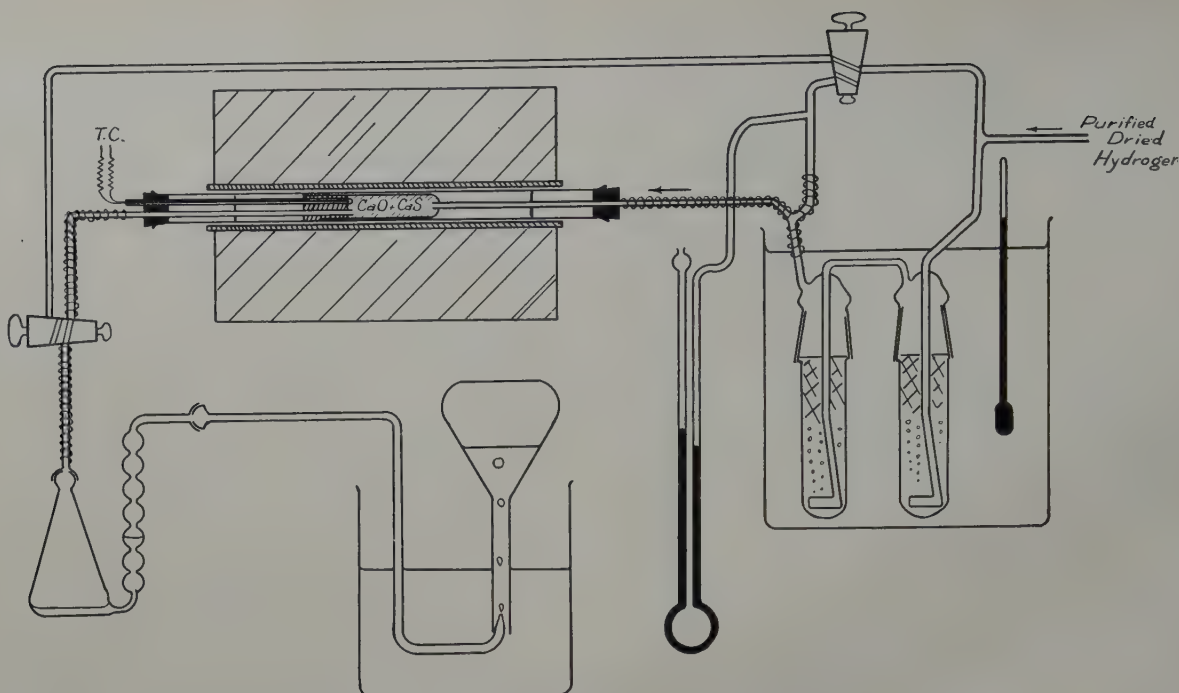


Fig. 1—Apparatus for study of the equilibrium  $\text{CaS} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S}$ .

vestigation the flow rate was kept between 50 and 80 cc per min.

Fig. 3 shows that when the  $\text{H}_2\text{O}/\text{H}_2$  ratio was varied over a wide range the  $\text{H}_2\text{S}/\text{H}_2$  ratio varied proportionally. This shows that the hydrogen sulphide in the outgoing gas actually is formed by the proposed reaction.

A thermocouple was inserted in the reaction mixture and the measurements were made from  $750^\circ$  to  $1425^\circ\text{C}$ . At the highest temperature a slight slagging was observed on the contact between the thermocouple and the reaction mixture, but without affecting the bulk of the mixture.

### Experimental Results

The experimental results listed in Table 1 represent the average of from two to five single analyses for each temperature. In Fig. 4 the logarithm of the gas ratio is plotted vs.  $1/T$ .

For the reaction  $\text{CaS}(s) + \text{H}_2\text{O}(g) = \text{CaO}(s) + \text{H}_2\text{S}(g)$ , the enthalpy is:

$$\Delta H = 15,650 \text{ cal}$$

and Gibbs free energy:

$$\Delta F^\circ = 15,650 - 0.87 \cdot T \text{ cal}$$

These values apply to temperatures between  $750^\circ$

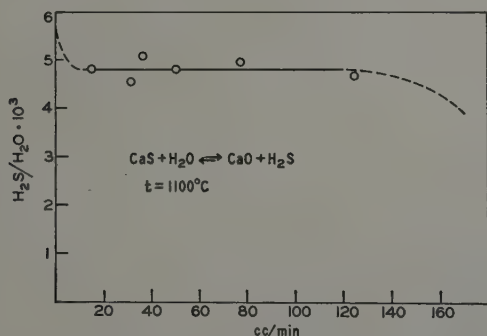


Fig. 2—Effect of flow rate on the ratio  $\text{H}_2\text{S}/\text{H}_2\text{O}$ .

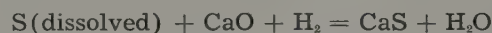
The dotted lines indicate the expected effects of thermal diffusion at low flow rates, and incomplete reaction at high flow rates.

and  $1425^\circ\text{C}$ , but as  $\Delta C_p$  of the reaction is small, they are assumed valid up to steelmaking temperatures of about  $1600^\circ\text{C}$ .

In this temperature range the free energy is about 3 kcal higher than that calculated from Osborn's free energy survey.\*

### Desulphurization of Liquid Copper

The escaping tendency of sulphur dissolved in a molten metal may be expressed conveniently by the equilibrium  $\text{H}_2\text{S}/\text{H}_2$  ratio which can be determined from the reaction:  $\text{S}(\text{dissolved}) + \text{H}_2 = \text{H}_2\text{S}$ . If this reaction is combined with the reaction  $\text{CaO} + \text{H}_2\text{S} = \text{CaS} + \text{H}_2\text{O}$ , one obtains:



As for low concentrations, the sulphur activity is closely proportional to the sulphur concentration, the sulphur content of a melt in equilibrium with solid calcium oxide and solid calcium sulphide will be closely proportional to the ratio  $\text{H}_2\text{O}/\text{H}_2$  in the atmosphere.

In order to see if this relationship actually holds, the desulphurization of liquid copper with lime was investigated. It was hoped in that way to obtain

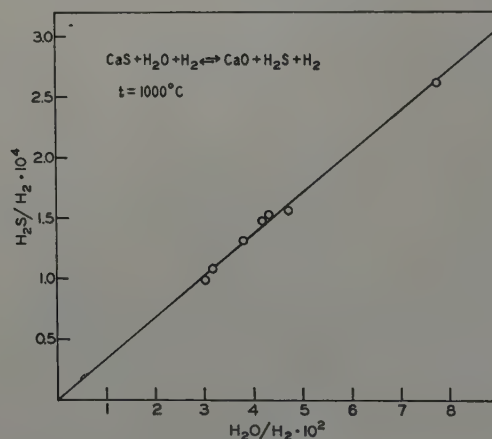


Fig. 3—Correlation between  $\text{H}_2\text{O}/\text{H}_2$  and  $\text{H}_2\text{S}/\text{H}_2$  ratio.



some information that might be useful for an understanding of the factors affecting the desulphurization of iron and steel. The principles behind the reaction would be the same for copper as for iron.

Hydrogen, saturated with water vapor at various temperatures, was bubbled through a copper melt in contact with solid CaO and solid CaS until equilibrium between the gas, the liquid, and the solid phases was established, Fig. 5. All runs were made at 1200°C. Most of the runs were carried out with about 50 g copper of 1.5 to 2.5 pct initial sulphur content and 3 to 5 g calcium oxide. Calcium sulphide then was formed during the reaction. A few preliminary runs, No. 12 and No. 16 (Table II), were made with a smaller amount of pure copper in contact with a larger amount of CaO and CaS. These runs gave results in agreement with the rest of the work. In all cases crucibles of zirconium silicate were used.

The amount of oxygen introduced in the copper melt by this procedure can be calculated from the recent investigation by Girardi and Siebert.<sup>6</sup> At 1200°C the oxygen concentration expressed in weight percentage will about equal  $H_2O/H_2 \cdot 10^{-4}$ . As in the present work the ratio  $H_2O/H_2$  was maintained between 1/20 and 1/2, the oxygen content will be of the order of  $10^{-5}$  pct. It is assumed that this will have no significant effect on the activity coefficient of sulphur in the melt.

Samples were drawn from the liquid copper by means of an arrangement similar to that used by Hatch and Chipman.<sup>7</sup> In order to prevent air from leaking into the apparatus when the sampler was inserted or removed, the tube was flushed with nitrogen during these operations, Fig. 5. The entire sample, 2 to 5 g, was dissolved in nitric acid and bromine and, after removal of the copper by electrolysis, sulphur was determined by precipitation as  $BaSO_4$ .

In some cases X-ray diffraction diagrams were taken of the crust of solids that remained in the crucible after the copper had been poured out. Invariably the lines of CaO and CaS were found proving that these compounds were present in their standard state.

In Fig. 6 the approach to equilibrium is studied as a function of time for a sequence of different gas compositions. Even if the scattering of the points is large, it is evident that there is no systematic trend with time after 5 hr of constant gas composition. Furthermore, Fig. 6 shows that the sulphur content is established equally well from the high as from the low side. It is therefore concluded that equilibrium values are established in about 5 hr, and in Table II are listed the results of various runs based on samples drawn after 5 to 29 hr of constant gas composition. The values were obtained about equally by approach from the high as from the low side.

During the reaction a small amount of hydrogen sulphide is formed, corresponding to the equilibrium  $H_2S/H_2$  ratio. This causes a removal of sulphur from the copper melt, a loss which has to be replenished by transfer of sulphur from the "slag." Equilibrium can only be expected when a significant amount of CaS remains, and when the rate of transfer between the slag and the metal is higher than the rate at which sulphur is removed as hydrogen sulphide. The general agreement between the values obtained by approach from both sides indicates that this is the case. Furthermore, the rate of sulphur removal

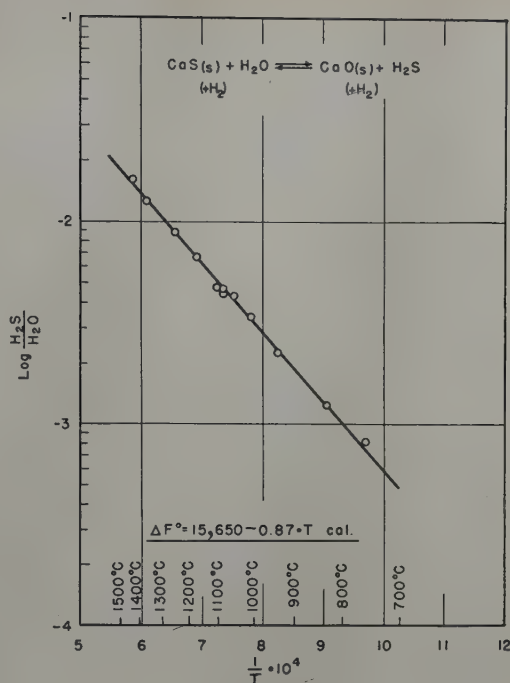


Fig. 4—Log  $H_2S/H_2O$  against  $1/T$ .

can be estimated from the  $H_2S/H_2$  ratio and the gas flow and, in the present case, is between 0.002 and 0.02 g per hr. This appears to be considerably less than the rate of sulphur transfer between the copper melt and the "slag" as estimated from the rate at which equilibrium is approached, Fig. 6.

Nevertheless, a certain instability is introduced due to the continuous removal of sulphur as hydrogen sulphide. This instability may be one of the reasons for the scattering of points in Figs. 6 and 7.

Fig. 7 shows that for less than 1 pct S the sulphur content of the copper melt is closely proportional to the ratio  $H_2O/H_2$ . The scale on the right hand side of Fig. 7 gives the corresponding  $H_2S/H_2$  ratio calculated from the data given in Table I.

The equilibrium  $S(\text{in Cu}) + H_2 = H_2S$  was investigated recently by Sudo.<sup>8</sup> For a temperature of 1200°C his data give an equilibrium ratio

$$\frac{H_2S}{H_2 \cdot \%S} \text{ equal to about } 4.5 \cdot 10^{-3}, \text{ valid for sulphur}$$

contents up to 0.87 pct. As seen from Fig. 7 this value is in very good agreement with the results of the present investigation.

For molten copper in equilibrium with molten cuprous sulphide Schuhmann and Moles<sup>9</sup> have found the  $H_2S/H_2$  ratio equal to  $4.2 \cdot 10^{-3}$  at 1200°C. According to Fig. 7 this should correspond to a maximum solubility of about 1 pct S in liquid copper. This is about half the solubility that is generally

Table I. Experimental Results

| Analysis Number | Temperature, °C | $H_2O/H_2 \cdot 10^2$ | $H_2S/H_2 \cdot 10^4$ | $H_2S/H_2O \cdot 10^2$ |
|-----------------|-----------------|-----------------------|-----------------------|------------------------|
| 44-49           | 1103            | 4.39                  | 2.11                  | 0.481                  |
| 53-55           | 1251            | 4.58                  | 4.06                  | 0.887                  |
| 56-57           | 940             | 7.42                  | 1.73                  | 0.233                  |
| 58-59           | 1081            | 7.38                  | 3.50                  | 0.475                  |
| 60-61           | 1081            | 4.53                  | 2.00                  | 0.442                  |
| 62-63           | 1067            | 4.38                  | 1.91                  | 0.436                  |
| 64-66           | 758             | 9.01                  | 0.74                  | 0.082                  |
| 67-68           | 832             | 8.66                  | 1.07                  | 0.124                  |
| 69-70           | 1002            | 4.63                  | 1.59                  | 0.343                  |
| 71-72           | 1176            | 4.63                  | 3.10                  | 0.670                  |
| 73-75           | 1350            | 4.67                  | 6.15                  | 1.317                  |
| 76-77           | 1425            | 5.34                  | 8.87                  | 1.66                   |

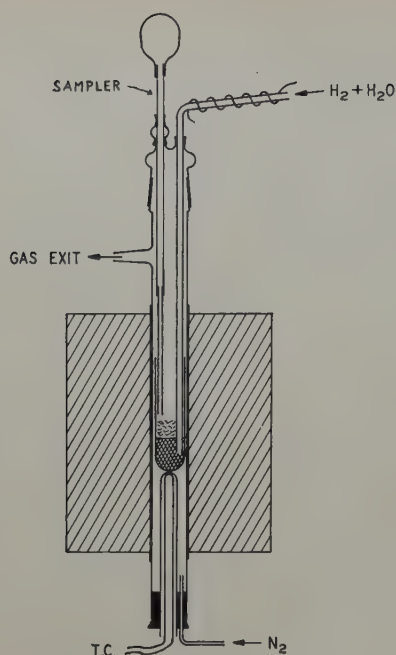


Fig. 5—Apparatus for study of copper desulphurization.

accepted.<sup>10</sup> In order to verify this finding, extended work by this and other methods have to be made.

#### Application to Blast Furnace Desulphurization

In a recent careful study, Hatch and Chipman<sup>7</sup> determined equilibrium values for the distribution of sulphur between carbon-saturated iron and various blast furnace slags in an atmosphere of pure CO. These authors were unable, however, to correlate their results with any theoretically calculated distribution coefficient. This may be due partly to insufficient knowledge about the activities of various constituents in the slag.

In this section Hatch and Chipman's data will be used, in connection with the data obtained in the present investigation, to calculate activity data for the slag.

If the reaction  $\text{CaS} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S}$  is combined with the water gas reaction  $\text{H}_2\text{O} + \text{C} = \text{H}_2 + \text{CO}$  to give:

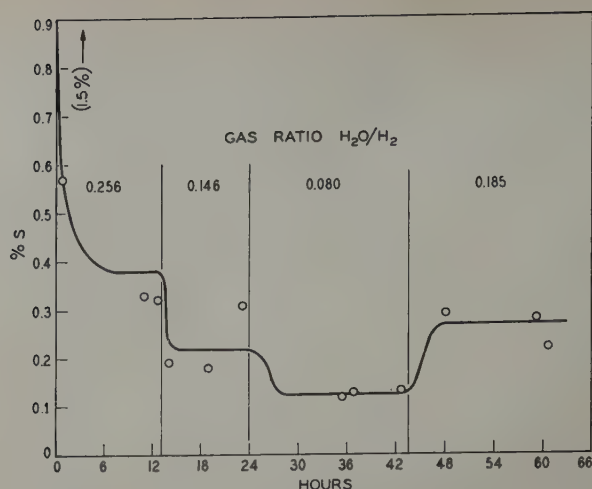


Fig. 6—Effect of time on the sulphur content of the copper melt.

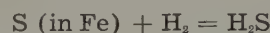
The horizontal levels given for each gas composition correspond to the sulphur values given by the curve on Fig. 7.



then

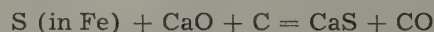
$$\Delta F^\circ = 17,210 - 34.09 \cdot T \text{ cal}$$

is obtained. The escaping tendency of sulphur in liquid iron is given by Sherman, Elvander, and Chipman:<sup>1</sup>



$$\Delta F^\circ = 9,840 + 6.54 \cdot T \text{ cal}$$

The reference state for sulphur here is chosen to be an ideal 1 pct solution of sulphur in pure iron. For the reaction:



therefore is obtained:

$$\Delta F^\circ = 27,050 - 27.55 \cdot T \text{ cal}$$

or at a temperature of 1500°C:

$$K = \frac{a_{\text{CaS}} \cdot p_{\text{CO}}}{a_{\text{CaO}} [\text{S}] \cdot f_{\text{S}} \cdot a_{\text{C}}} = 490$$

Under the conditions studied by Hatch and Chipman  $p_{\text{CO}}$  and  $a_{\text{C}}$  were both unity. For iron saturated with carbon at 1500°C, Morris and Buehl<sup>2</sup> found the activity coefficient  $f_{\text{S}}$  equal to about 5.8.

This gives for a system in equilibrium with graphite and a CO atmosphere:

$$\frac{a_{\text{CaS}}}{a_{\text{CaO}}} = 2842 \cdot [\text{S}]$$

The activities  $a_{\text{CaS}}$  and  $a_{\text{CaO}}$  are referred to the pure solids as standard state, and  $[\text{S}]$  is the sulphur content of the iron melt in weight percentage.

The activity of calcium oxide in a calcium silicate melt can be approximately derived from the free energy diagram of the system  $\text{CaO-SiO}_2$  given by Darken.<sup>11</sup> For a melt with the ratio  $\text{CaO/SiO}_2 = 1$ ,  $a_{\text{CaO}} \approx 0.010$  and for a melt with  $\text{CaO/SiO}_2 = 1.5$ ,  $a_{\text{CaO}} \approx 0.025$ . In Table III these values are combined with sulphur distribution data obtained by Hatch and Chipman and values for  $a_{\text{CaS}}$  are calculated.

In Fig. 8 the activity of CaS is plotted vs. the sulphur content of the slag, (S). For both types of slag the activity may be represented adequately by one single curve. The activity seems to reach unity at about 10 pct S. This value agrees rather well with McCaffery and Oesterle's<sup>12</sup> experimental values

Table II. Desulphurization of Molten Copper

| Sample Number | H <sub>2</sub> O/H <sub>2</sub> | Wt Pct S | Sample Number | H <sub>2</sub> O/H <sub>2</sub> | Wt Pct S |
|---------------|---------------------------------|----------|---------------|---------------------------------|----------|
| 12            | 0.418                           | 0.65     | 50            | 0.078                           | 0.16     |
|               |                                 |          | 51            | 0.079                           | 0.14     |
| 16            | 0.192                           | 0.33     | 56            | 0.184                           | 0.26     |
| 21            | 0.256                           | 0.33     | 57            | 0.184                           | 0.27     |
| 22            | 0.257                           | 0.32     |               |                                 |          |
|               |                                 |          | 59            | 0.245                           | 0.31     |
| 23            | 0.145                           | 0.19     | 63            | 0.038 <sub>s</sub>              | 0.07     |
| 24            | 0.146                           | 0.18     | 64            | 0.038 <sub>s</sub>              | 0.08     |
| 25            | 0.148                           | 0.31     | 65            | 0.043 <sub>7</sub>              | 0.09     |
| 26            | 0.080                           | 0.12     | 66            | 0.043 <sub>8</sub>              | 0.08     |
| 27            | 0.080                           | 0.13     |               |                                 |          |
| 28            | 0.079                           | 0.13     | 68            | 0.058 <sub>5</sub>              | 0.08     |
| 29            | 0.187                           | 0.29     |               |                                 |          |
| 30            | 0.183                           | 0.28     | 76            | 0.512                           | 1.0—     |
| 31            | 0.185                           | 0.22     | 77            | 0.527                           | 0.95     |
|               |                                 |          | 82            | 0.340                           | 0.57     |
| 33            | 0.138                           | 0.18     | 84            | 0.348                           | 0.48     |
| 34            | 0.138                           | 0.22     |               |                                 |          |
| 37            | 0.059                           | 0.09     | 87            | 0.253                           | 0.30     |
|               |                                 |          | 88            | 0.260                           | 0.45     |



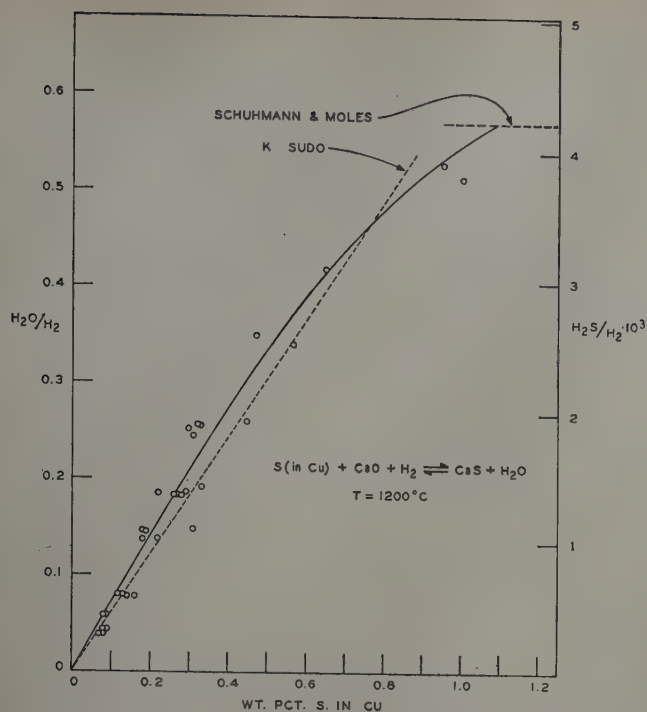


Fig. 7—Sulphur in molten copper as a function of the ratio  $H_2O/H_2$ .

The right hand scale gives the corresponding  $H_2S/H_2$  values.

for the solubility of CaS in various blast furnace slags. These authors found the CaS solubility at  $1500^\circ\text{C}$  to vary from about 8 pct S for acid slags to about 11 pct for the more basic slags. Glaser<sup>13</sup> found the solubility of CaS in a pure  $\text{CaSiO}_3$  melt corresponding to 5.5 pct S at  $1500^\circ\text{C}$ . Furthermore Glaser showed that at a somewhat higher sulphur content and temperature a region of liquid immiscibility occurred. This means that  $a_{\text{CaS}}$  would be expected to show a pronounced positive deviation from ideality. This is confirmed by Fig. 8.

The agreement between the activity data given in Fig. 8 and the activities to be expected from solubility data actually confirms the values for  $a_{\text{CaO}}$  which with considerable uncertainty were derived from Darken's free energy diagram.

If the slag had contained an excess of solid CaS,  $a_{\text{CaS}}$  would be unity and at  $1500^\circ\text{C}$ :

$$a_{\text{CaO}} = \frac{3.52}{[\text{S}]} \cdot 10^{-4}$$

An experimental determination of the sulphur content of the iron melt under these conditions may give us a possible way to determine activity values for CaO in slags of various compositions and basicities.

The general conclusion of this investigation is that the activity of sulphur in a molten metal in equilibrium with a slag will be proportional to the atomic oxygen fugacity in the system, expressed by

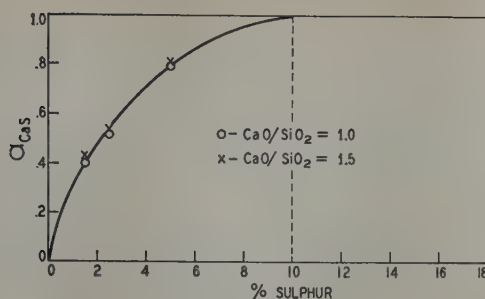


Fig. 8—Activity of CaS in blast furnace slags.

the ratio  $H_2O/H_2$ ,  $\text{CO}_2/\text{CO}$ , or  $\text{CO}/a_{\text{O}}$ , and proportional to the ratio  $a_{\text{CaS}}/a_{\text{CaO}}$  in the slag. The activities  $a_{\text{CaO}}$  and  $a_{\text{CaS}}$  are exactly defined quantities and do not correspond to any assumed picture of "free lime" or "sulphur combined with calcium."

Most probably liquid slags are highly ionized and, for the lack of any dissociation constants, activities can be defined for the sulphur and oxygen ions, so that:

$$\frac{a_{\text{CaS}}}{a_{\text{CaO}}} = \frac{a_{\text{S}^{2-}}}{a_{\text{O}^{2-}}}$$

If the ratio between the activity  $a_{\text{S}^{2-}}$  and percentage of sulphur in the slag (S) is called  $\gamma_{\text{S}^{2-}}$ , it will be seen that the amount of sulphur a given slag will absorb under a given oxygen and sulphur fugacity will be proportional to  $a_{\text{O}^{2-}}/\gamma_{\text{S}^{2-}}$ .

This quantity can be called the sulphur-capacity of the slag. It is a fundamental, intrinsic property of the slag, the detailed knowledge of which would be of considerable importance. This quantity may be determined experimentally by passing a controlled mixture of hydrogen, hydrogen sulphide, and water vapor through the molten slag and determining the equilibrium sulphur content (S). The relation then will be:

$$\frac{a_{\text{O}^{2-}}}{\gamma_{\text{S}^{2-}}} = K \cdot \frac{H_2O}{H_2S} (S)$$

K is equal to the equilibrium constant for the reaction  $\text{CaS} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S}$ , as given in Table I and Fig. 4.

A research program along these lines is planned.

### Summary

The desulphurizing power of calcium oxide in its standard state has been investigated.

1—The reaction  $\text{CaS} (s) + \text{H}_2\text{O} (g) = \text{CaO} (s) + \text{H}_2\text{S} (g)$  has been studied from  $750^\circ$  to  $1425^\circ\text{C}$ . The Gibbs free energy of the reaction can be expressed as follows:

$$\Delta F^\circ = 15,650 - 0.87 \cdot T.$$

See Table I and Fig. 4.

2—The desulphurization of liquid copper with calcium oxide has been studied at  $1200^\circ\text{C}$ . It is found that the sulphur content in the copper is closely proportional to the  $H_2O/H_2$  ratio in the atmosphere, as would be expected in accordance with the equation:



The results indicate a maximum solubility of sulphur in liquid copper at  $1200^\circ\text{C}$  of about 1 wt pct, Table II and Fig. 7.

3—The obtained data for the desulphurizing power of calcium oxide have been combined with blast furnace desulphurization data, obtained by

Table III. Activities in Calcium Silicate Slags

| CaO/SiO <sub>2</sub> = 1, $a_{\text{CaO}} \approx 0.010$ |            |                                         |                  | CaO/SiO <sub>2</sub> = 1.5, $a_{\text{CaO}} \approx 0.025$ |            |                                         |                  |
|----------------------------------------------------------|------------|-----------------------------------------|------------------|------------------------------------------------------------|------------|-----------------------------------------|------------------|
| (S)<br>pct                                               | (S)<br>[S] | $\frac{a_{\text{CaS}}}{a_{\text{CaO}}}$ | $a_{\text{CaS}}$ | (S)<br>pct                                                 | (S)<br>[S] | $\frac{a_{\text{CaS}}}{a_{\text{CaO}}}$ | $a_{\text{CaS}}$ |
| 1.5                                                      | 107        | 39.8                                    | 0.398            | 1.5                                                        | 250        | 17.1                                    | 0.426            |
| 2.5                                                      | 140        | 51.2                                    | 0.512            | 2.5                                                        | 335        | 21.3                                    | 0.533            |
| 5.0                                                      | 180        | 79.6                                    | 0.796            | 5.0                                                        | 440        | 32.4                                    | 0.810            |

Hatch and Chipman,<sup>7</sup> and with calcium oxide activity data obtained from Darken's free energy diagram of the system CaO-SiO<sub>2</sub>.<sup>11</sup> Values for  $a_{\text{CaS}}$  are calculated for slags of various basicities and sulphur contents, Table III and Fig. 8.

With emphasis on the ionic theory for liquid slags the expression  $\frac{a_{\text{CaO}} \cdot S}{a_{\text{CaS}}} = \frac{a_{\text{O}^{2-}}}{\gamma_{\text{S}^{2-}}}$  is suggested as a measure for the sulphur capacity of the slag.

### Acknowledgments

The first part of this work was carried out with the help and assistance of E. M. Cox, the second part with assistance of B. L. Dunicz. Their help is thankfully acknowledged. The copper-sulphur samples were analyzed by Miss M. C. Bachelder, Mrs. E. W. Nobile and A. A. Roman; thanks are due to them.

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### Technical Note

## Effect of Hardness on Temper Brittleness

by D. C. Buffum and L. D. Jaffe

QUANTITATIVE measurements of the temper brittleness of steel are made by comparing the difference between embrittled and unembrittled specimens in the temperature of transition from ductile to brittle fracture. Since hardness affects the transition temperature, a study of the combined effects of hardness and temper brittleness appeared desirable.

In this investigation a commercial SAE 3140 steel, which has been reported on previously in temper brittleness studies,<sup>\*</sup> was used. Blanks from this steel were austenitized for 1 hr at 900°C and water quenched. The blanks were then divided into six groups and further heat treated as follows: Group 1—tempered at 675°C for 4 hr and water quenched; Groups 2, 3, 4, and 5—tempered at 675°, 650°, 625°, and 600°C respectively for 1 hr and water quenched; and Group 6—tempered at 500°C for ½ hr and water quenched.

Each of these groups was divided into two parts; one part was tested without further heat treatment, and the other was embrittled for 48 hr at 500°C and water quenched. Tempering treatments between 500° and 600°C were avoided because of the rapid embrittlement occurring in that range for this steel.

The heat-treated blanks were machined into standard V-notched Charpy bars. Each group was tested over a range of temperatures on a 217 ft-lb Charpy machine.

The energies necessary to fracture the bars and the percentage fibrous fracture of each bar were recorded. The transition temperatures were obtained from a plot of the percentage fibrous fracture as a function of testing temperature. They were taken as the lowest point on these curves at which the fracture was 100 pct fibrous. The transition temperatures for both embrittled and unembrittled

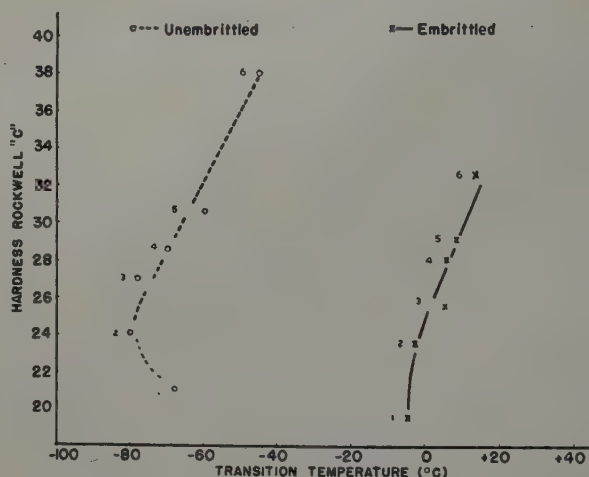


Fig. 1—Transition temperature as a function of hardness. Numbers indicate heat treatment groups.

specimens are presented in Fig. 1 as function of the hardness. It will be noticed in this figure that the point for the unembrittled condition at 21 Rockwell C is out of line. These specimens were tempered for 4 hr at 675°C and this point indicated that under isothermal conditions at this temperature, as is well known, embrittlement may develop fast enough to more than offset the effects of softening.

From this data, it was concluded that the difference between transition temperatures for the embrittled and unembrittled conditions at any given hardness, within the range of Rockwell C 24½ to 32½, is constant.

It is also concluded that, within the hardness range studied, the transition temperatures for embrittled and unembrittled specimens rise in a parallel fashion with an increase in hardness.

The authors wish to acknowledge the assistance of Frank Carr in this work.

D. C. BUFFUM, Junior Member, and L. D. JAFFE, Member AIME, are associated with the Watertown Arsenal, Watertown, Mass.  
 TN 82E. Manuscript, April 23, 1951.

\* L. D. Jaffe and D. C. Buffum: Isothermal Temper Embrittlement. *Trans. ASM* (1950).



# Discussion — Institute of Metals Division\*

Chicago Meeting, October 1950

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\* TP 3090E

## An Experimental Survey of Deformation and Annealing Processes in Zinc

by D. C. Jillson

### DISCUSSION, B. Averbach presiding

**J. R. Lane** (*Metals Research Laboratory, Washington*)—A new type of deformation called “kinking” has recently been described. Is there any relation between the “rumpling” described in this paper and “kinking?”

**D. C. Jillson** (author's reply)—Both are manifestations of bending about [210] axis. The difference is one of degree.

**W. C. Ellis** (*Bell Telephone Laboratories, New York*)—Some observations of deformation in zinc recorded in this paper may be applicable generally to flow in metals. One of these, deformation in torsion without evidence of slip or twinning in the early stages and with startling ease, when the twist is about the hexagonal axis, adds another method of flow to the presently increasing list of mechanisms. This illustrates again that a crystal will utilize any realizable process to flow and relieve stress. The process is not necessarily classical directional slip—in this case, it is rotational slip. The question naturally occurs: Will face-centered cubic metals stressed by twisting about an octahedral axis flow in a similar manner by rotation on an octahedral plane? I would like to ask Dr. Jillson if he has

made any experiments or knows of any experiments of this type on face-centered cubic metals? Face-centered cubic metals possibly would behave differently from zinc, since, for one thing, the stacking sequence is different for the two structures. The results of such experiments, however, would be instructive in providing more information about deformation processes.

**D. C. Jillson**—Dr. Roy E. Swift, working in the Hammond Laboratory at Yale, performed a twist test on a single crystal of brass. The work has not been published, and I do not know the crystallographic direction of the axis of the specimen used.

**Lo-ching Chang** (*Columbia University, New York*)—Observations similar to Figs. 1 and 2 of the paper were obtained by us during the bending and unbending of an orthorhombic Au-Cd alloy.<sup>51</sup> This orthorhombic alloy is the product of diffusionless transformation from a single crystal of  $\beta$  Au-Cd alloy (CsCl structure) containing 47.5 atomic pct Cd on cooling to about 60°C.<sup>52</sup> Referring to the effects of annealing, has the author tried any long time high temperature anneal, such as 150 to 200 hr at 400°C?

**D. C. Jillson**—No.

**C. Crussard** (*Ecole des Mines, Paris, France*)—I



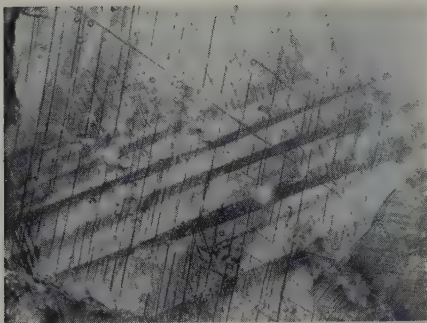


Fig. 16—Grain at the surface of a uranium polycrystal compressed 2 pct, showing twinning, slip, and kink bands. The kink bands are the broad markings. X100.

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would like to mention a few observations on the twinning and detwinning of a zinc crystal, which I made<sup>53</sup> and which are in agreement on many points with those of Dr. Jillson. The crystal was made by recrystallization, which is rather easy with impure zinc, but becomes more difficult, the purer the metal; as I have explained elsewhere,<sup>55</sup> with the 99.99 pct Zn used, it was very difficult to prepare single crystals by this method; only three were obtained.

One crystal had an orientation with the basal plane parallel to the axis of the specimen. This made it unsuitable for elongation; but it could easily twin by torsion. The twin was studied by torsion under the microscope. As observed by Dr. Jillson, a rather strong torque had to be applied to make the twin start, with a click; after which, the twin grew under a very small torque, without hardening. Reversal of the stress caused progressive detwinning, under a small torque, until a faint line only was visible. But this last trace did not disappear; under a new reversal of stress it could grow again under a small torque, as the first time. The operation could be repeated.

When a fine line was left, it could disappear (with a click) under a strong (reverse) torque, of the same order as that necessary to initiate the twin. After complete disappearance of the twin, when I tried to produce a new twin, it started in another place. Thus it seems that the "nucleus" of a twin is hard to produce; but once produced, it has an appreciable stability.

The "rumpling" shown by the author is very interesting. It can be interpreted as a polygonization during deformation. The latter has been observed in my laboratory<sup>54</sup> in all types of deformation in aluminum; it is very strongly developed during creep. In other words, dislocations show two competitive trends: To cluster in walls, or to trigger "avalanches," if they have enough kinetic energy. The latter factor is the key to the whole problem.

**D. C. Jillson**—It is difficult to grow strain-anneal single crystals of high-purity zinc, as reported by Mathewson and Phillips.<sup>56</sup> We found at that time that a critical content and, perhaps, dispersion of iron was helpful.

Regarding detwinning, it seems likely that the conditions in Professor Crussard's torsion specimen were not so simple as those in some of our specimens and that his inability to detwin them completely without an increase in stress may have been due to this. We were frequently unable to detwin completely in specimens where the deformation was more extensive.

**R. W. Cahn** (Ministry of Supply, Atomic Energy Research Establishment, Harwell, Berks, England)—Dr. Jillson's observations on the widespread prevalence of glide-plane bending in zinc will, I am sure, assist considerably towards a complete understanding of the plastic behavior of metals. What is particularly interesting is the apparently general tendency for uniform curvature in a lattice to turn into a segmented or "polygonized" curvature. This is brought out by the X-ray photographs in the paper which show that a

segmented curvature exists in a zinc crystal immediately after bending, albeit on a very fine scale. This observation is also in line with Ramsey's observations<sup>58</sup> on the cell structure of polycrystalline zinc extended at room temperature. I have found what is almost certainly an instance of the same phenomenon both in stretched and in compressed polycrystalline uranium, Fig. 16. Here there are pairs of bend planes, of opposite sense, approximately normal to the slip direction, just as in the cases illustrated by Jillson: These pairs constitute "kink bands."

It seems to me that in all these cases, the basic phenomenon is that of the single bend plane. A kinked zinc crystal contains numerous such planes of both senses, combined with sharp continuous curvature, while a bent crystal, according to Dr. Jillson, contains a very large number of feeble bend planes of the same sense. The so-called deformation bands in aluminum, studied at Yale University, by Honeycombe,<sup>57</sup> and by myself among others, are probably constituted by pairs of bend planes, as recently suggested by Mathewson.<sup>58</sup> Fig. 17 is a photograph of such a band in aluminum. It was generally found, as here, that one side of the band was more sharply curved than the other. The occurrence of such bands formed in tension, and kink bands in zinc formed by compression, are not consistent with Dr. Jillson's picture suggested at the end of his paper. He proposes that bands are formed and disappear again periodically, each such cycle being associated with a sort of slip quantum. In the cases just cited, however, the bend planes, once created, form a permanent barrier in the lattice: They become progressively sharper, each acting as a sieve in retaining dislocations of one sign. The effect of annealing seems to be to sharpen the curvature. This may happen by a segmentation of an apparently continuous curvature, as in Fig. 18, which was made from a deformation band in an aluminum crystal annealed after extension, repolished after annealing, and then slightly stretched again; or it may happen by a coalescence of segments already existing, as would appear to be the case when a bent zinc crystal is annealed. The motion of dislocations involved in such processes can be very considerable and may be evidenced by a visible change in the shape of a specimen on annealing. Thus Fig. 19 is a photograph of the surface of an aluminum crystal which was stretched with the generation of deformation bands, repolished, and then annealed. The anneal brought about the change of structure also shown in Figs. 17 and 18, but here this change revealed itself by a marked rumpling on the previously smooth surface. (Figs. 17 and 18 are sections almost parallel to the slip direction, Fig. 19 a section inclined to this direction.) This rumpling distinguishes the process in question from grain boundary migration, which generally does not affect the specimen surface, except for minor effects attributed to thermal etching.

This suggests that dislocation models of grain

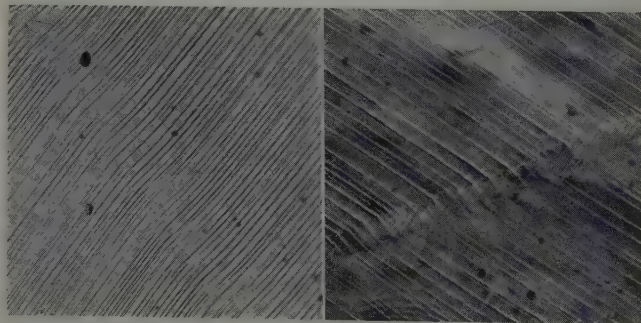


Fig. 17 (left)—Deformation or kink band in an aluminum crystal stretched 24 pct. X250.

Fig. 18 (right)—Aluminum crystal stretched 31 pct, annealed 1 hr at 450°C, repolished and slightly stretched. X260.

Areas reduced approximately 66 pct for reproduction.



boundaries should be re-examined, since on the basis of such a model boundary migration in a specimen should affect its shape, just as polygonization of a deformation band does. The motion of a plane array of dislocations normal to itself is in fact equivalent to a shear. Fig. 20 shows this in an exaggerated fashion, and also shows how such a shear would be expected to occur under the action of an applied shear stress. Experimental data on this point might be rather informative. Indirect evidence that applied stress accelerates the motion of dislocation arrays can be found in recent experiments on creep.<sup>69, 70</sup> It was found that during the creep of aluminum, the lattice became segmented into mutually inclined "cells." This process also occurs, in the way described above, if a specimen is stretched rapidly and then annealed without applied stress, but in the latter case the segmented structure develops more slowly.

The marked effect of applied stress on polygonization is brought out clearly by the following experiment. Two specimens were cut from adjacent portions of a large crystal of aluminum which had been stretched by 20 pct, and all surfaces on both specimens were prepared metallographically. The two specimens then were placed side by side for 1 hr in a furnace at 445°C, one being subjected to a small tensile stress of 100 g per sq mm, and the other not stressed. The stressed specimen exhibited very strong surface rumplings as in Fig. 19, while the markings on the unstressed specimen were so feeble as to be scarcely visible; and this difference existed though the stress was too low to cause any trace of slip.

It is evident enough that slip is associated almost universally with the bend planes to which Dr. Jillson has redirected attention. This makes it interesting to speculate why they do not occur in certain specific cases, such as the extension of single crystals of zinc or cadmium, or of aluminum crystals of certain orientations.<sup>68</sup> I should be most interested to know Dr. Jillson's views on this problem.

Perhaps the cases just mentioned, and the instances of strongly developed deformation bands, are simply opposite extremes of a general process on the lines proposed by Dr. Jillson, i.e., in some cases deformation bands form cumulatively, in others they begin to form all the time but are constantly straightened out again. This view is strengthened by the observations that in an aluminum crystal stretched by, say, 30 pct, the strongly marked deformation bands are accompanied by numerous incipient bands which are too weak to be visible on the surface of the stretched crystals, but are rendered visible on the repolished surface by annealing.

Dr. Jillson's observations on twinning are also most elegant and striking. The thickness vs. time curves determined for the growth of deformation twins in zinc prompt several questions. Dr. Jillson accounts for the form of these curves in terms of an energy hump required to nucleate the twin which will grow catastrophically once it is nucleated because of the reduced

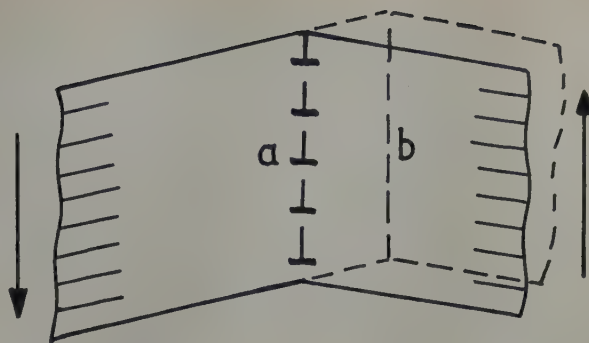


Fig. 20—Initial (a) and final (b) position of a bend plane subjected to a shear stress, schematic.

resistance to growth. The gradual slowing down of the growth in thickness is held to be due to the progressive relief of the stress which brought the twin into existence. But this view implies the use of a stiff spring to apply the force (a vice is effectively equivalent to this), the force in which is reduced as the specimen gives way. On the picture as stated, a twin should grow continuously to an unlimited extent under conditions of dead loading, for then no amount of twinning can relieve the stress, and a particular twin might be expected to continue growing more readily than another would be nucleated. At any rate, it would be expected that the thickness vs. time curve would have a different form in this case. It is an observed fact, however, that twins do not usually exceed a limiting thickness which varies with the particular metal. If this is followed up, it becomes apparent that there is a rough correlation between the characteristic widths of deformation twins in various metals and the shears associated with them. Thus in bismuth and tin in which the twins undergo a very small shear ( $s = 0.118$  and  $0.120$ , respectively), very coarse twins, a large fraction of a millimeter across, can be produced; while in  $\alpha$  iron, the twins, for which  $s = 0.707$ , never exceed a few microns in width, and in the face-centered cubic metals, for which the shear would be the same, deformation twins are chimeras, heard of but not seen. Now the higher the amount of shear, the more closely the atoms are forced together during the shearing process itself, and the higher the energy barrier to be overcome. It may well be that in the catastrophic first stage of the growth of a twin, cumulative strains are generated in the parent crystal adjacent to the growing twin and in the twin itself, and it may well be those stresses which set a limit to the growth of the twin. Other factors also will contribute to determining this limiting width (e.g., the closeness to which the twinning process approximates to a pure shear, which in turn depends on the crystal structure) and the correlation between this width and the shear is not perfect. Thus neither of the types of deformation twins in uranium (with shears of  $0.299$  and  $0.213$ ) ever exceed a few microns in width, though the shear is considerably less than for iron.

Another question which occurred to me is whether, when a twin is formed and destroyed repeatedly by reversing the stress, the twin always appeared in exactly the same plane and grew to the same thickness for a particular stress. If this was so, it would imply either that not all vestiges of the twin disappeared during the reverse cycle (i.e., that the twin nucleus is as difficult to erase as it is to create), or else that the twin forms at a place where the lattice is disturbed prior to the application of the stress. Furthermore, the occurrence of bend planes at the tip of a lenticular twin, as sketched in Fig. 12, should lead to a building up of permanent strain in the crystal on reverse cycling (unless indeed the formation of such bands is perfectly reversible), and this might be expected to affect the appearance of the twin as the number of cycles increased.

Finally I should like to ask Dr. Jillson how he was able to detect the very interesting instances of bend

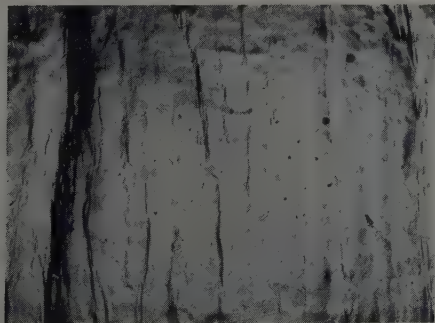


Fig. 19—Aluminum crystal stretched 35 pct, repolished and annealed 16 hr at 435°C (under a stress of 35 g per sq mm). X30.

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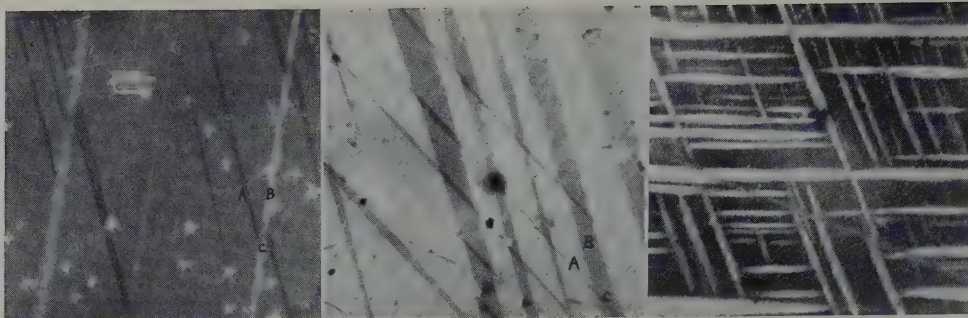


Fig. 21 (left)—Deformation twins in uranium section. Polarized light. X1500.

Fig. 22 (center)—Deformation twins in uranium section. Polarized light. X1200.

Fig. 23 (right)—Deformation twins in uranium section. Polarized light. X1200.

planes being associated with twin tips and intersections, Fig. 12. These observations go some way towards explaining something which has puzzled me for a long time, namely, how a lenticular twin can be formed at all. However, the bands must surely be extremely faint—I have certainly never been able to detect any at the extremities of twins in deformed uranium, though I am very ready to believe that they are there. It may incidentally be of interest to record here that places where twins intersect or abut on each other are not necessarily places of high strain. Figs. 21 and 22 show two fields in compressed grains of uranium, in which two families of twins cross each other with a fine disregard for each other's presence; this may be compared with Fig. 23, showing a different pair of twin families again, in which most of the twins stop short of each other in the way familiar in, say, bismuth. In the case of the smooth intersections, twins A and C intersect along a line lying in the plane of twin B, and moreover the direction and amount of shear is the same in both A and C. In the case of Fig. 21, this direction coincides with the intersection of A and C, and we have a phenomenon directly analogous to cross-slip, i.e., cross-twinning. Here twin B is formed by a shear of the first type.<sup>61</sup> In the other case, twin B is formed by a shear of the second type.<sup>61</sup> When the conditions mentioned above did not apply, the characteristic appearance of Fig. 23 was encountered.

I trust Dr. Jillson will forgive the somewhat disjointed nature of these remarks, which are put forward in the hope that they may return a tiny fraction of the stimulation which I have found in his own paper.

**D. C. Jillson**—The questions raised in your second and fifth paragraphs are answered, of course, in your sixth paragraph. I see no inconsistency between the formation and removal or flow of very slight, highly submicroscopic bends under stress and the piling up of such minute bends at a barrier of one kind or another to form a detectable bend. They might also pile up if conditions were such that the rate of formation exceeded the rate of flow. After the pile-up reaches a certain size, it might itself, as you suggest, present a barrier. I expect that in cases where deformation does not seem to result in bend planes we can assume that coalescence or piling up has not progressed to a point where the bends can be detected. If we were to deform a sufficiently perfect specimen under suitable conditions, piling up or large bends might be avoided, and bend planes might never be detected. Bend planes most certainly have been observed in single crystals of zinc extended under other conditions.

The problem is the same if you are thinking in terms of dislocations. To supply the number of dislocations required to account for plastic flow, assumptions of generation at the surface, or of reflection, or of multiplication have been made. I suggest that rumpling may afford a mechanism for the generation of dislocations within a crystal and that there seem to be reasons for giving serious attention to this possibility:

In regard to the thickness of mechanical twins, I expect that in the unattainable case of a perfect crystal

in a perfect setup, such that a single twin might form and grow without restraint and without the introduction of any other deformation, dead loading would cause unlimited growth without the nucleation of another twin. The rough correlation between widths of twins and the shears associated with twinning is probably a result of constraints, and I would expect the width of twin for a given metal to vary with the conditions determining the degree of constraint.

The question of whether a twin recurs on exactly the same plane upon repeated twinning and detwinning could not be answered experimentally because other deformations were always introduced. Had the specimen been perfect and had no other deformation been introduced, the shearing should have started between the planes where the stress was the highest, and if the experiment could have been carried out perfectly, this should have been the same place every time.

The specimen represented in the bottom sketch in Fig. 12 was obtained by compressing a smooth cylindrical specimen in which the basal plane was perpendicular to the specimen axis. The resultant markings were quite clear on the cylindrical surface. The markings of the middle sketch, too, were clear enough on the smooth surfaces of a deformed specimen of square section. The nature of the markings shown in the top sketch was deduced from observations of the markings on basal faces cleaved before the specimen was twinned. It was noted that if the twin went all the way through the specimen, there was no adjacent bend, but that if the twin did not, being then of a presumably lenticular shape, there was an adjacent bend in the surface. The sketch represents what we believe to be a logical rationalization. We did not observe this on a polished section such as shown in the sketch because the actual bend was very slight. The difference in the reflection of light from the basal surface, however, was quite definite.

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# A Study of the Plastic Behavior of High-Purity Aluminum Single Crystals at Various Temperatures

by F. D. Rosi and C. H. Mathewson

DISCUSSION, B. Averbach presiding

**P. A. Jacquet** (Paris, France)—The authors state on p. 1163: "It is known that the oxide film which forms very rapidly on electrolytically polished aluminum in contact with air has a disturbing effect on the appearance of slip bands, making them wavy rather than straight."

Actually the oxide layer which builds itself in the air on an aluminum surface electropolished in the proper way is extremely thin—it is not visible by electron diffraction as observed by H. Raether<sup>28</sup>—and cannot have any effect on the slip bands.

On the other hand it is well known that some polishing baths which contain fluoboric acid, phosphoric acid, nitric acid, etc., lead to the building up of a thick oxide layer during the polishing. Thus with such an electrolyte aluminum comes out of the bath already oxidized, whereas with a  $\text{ClO}_4\text{H}$ -acetic anhydride bath the metal is practically un-oxidized when taken out and then is covered rapidly with a 20A thick layer which subsequently grows very slowly.

G. R. Wilms has shown that the thick alumina layers built up during polishing in the above-mentioned electrolytes hinder the observation of aluminum surface deformation. He determined also that the same cause of error does not exist with a metal polish in perchloric acid-acetic anhydride bath.

**F. D. Rosi** (authors' reply)—Dr. Jacquet is quite right in pointing out that the difficulty encountered in observing deformation markings is a direct result of the oxide layer developed during the electrolytic polishing. It was not intended to attribute the degree of thickness of the oxide layer entirely to specimen contact with the atmosphere. In fact, it was mentioned in the paper that "the nature of the oxide film depends to a great extent upon the electrolytic polish used, and perhaps unintentional variations in the technique of polishing." From the observed results, we strongly believe that the oxide film resulting from polishing in a methyl alcohol-nitric acid bath is not deleterious to the observation of slip markings in high-purity aluminum. Like Dr. Jacquet, we, also, have found that polishing in a fluoboric acid bath makes the examination of surface markings difficult.

**N. K. Chen and R. Maddin** (Johns Hopkins University, Baltimore)—The results recorded in this paper are very interesting; in particular, we would like to refer to the authors' Fig. 10, in which is shown the effect of increasing strain on the density of slip bands in the early stages of plastic flow. Although it is apparent from the curves that the orientation of the crystals has a marked effect on the density of slip bands for a given amount of strain, no particular orientational relationship seems to have been established.

One of the discussers (N. K. Chen) has made a structural study of aluminum single crystals of many orientations after plastic extension. Most aluminum single crystals exhibit slip lines with a reasonable regularity of spacing, together with deformation bands. However, there is an area of orientation, spreading out from the  $\langle 111 \rangle$  pole of the Taylor and Elam triangle, in which flexural gliding seems not to occur and slip lines are spaced much more irregularly, assuming a strongly clustered appearance,<sup>29</sup> Fig. 23. By simple comparison it is apparent that crystals with clustered slip lines will give a smaller density of slip markings upon measurement.

Thus it is noticed that in the authors' Fig. 10 crystals G and E, which exhibit a much smaller number of slip bands per mm than the crystals T and H at the same amount of strain, are both oriented with their stress axes near  $\langle 111 \rangle$ , the particular area discussed above. Since strain hardening did not appear to vary with the

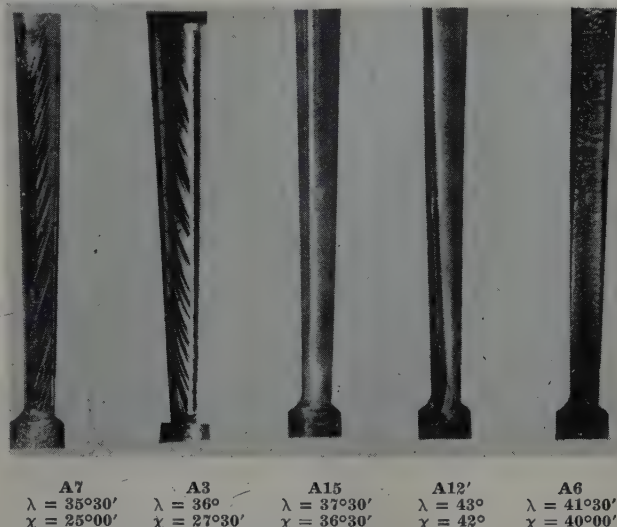


Fig. 23—Effect of orientation on distribution of slip bands on extended tapered aluminum single crystals. X1.

orientation of the crystal, and thus could not be used as a clue in this case to explain such fundamental difference of the appearance of slip bands, the nature of lattice rotations, such as the generation of deformation bands, and operations of conjugate and cross-slip systems, may be considered as one probable cause.

For example, it has been shown by Heidenreich<sup>30</sup> that in aluminum the glide lamellae are about 200A thick and have been displaced about 2000A. For equal amounts of strain it would appear that the displacement of lamellae must vary if the density of the slip bands is to change with the orientation.

If crystals such as the authors' G and I, extended the same amount, are to have a vastly different density of slip bands, then either the displacement of the bands in the different crystals in question must vary or other factors such as the action of collateral slip systems and the formation of deformation bands retard the classical lattice rotation of one of these crystals (the one having the greater number of slip bands), so that both result in the same amount of strain.

**F. D. Rosi**—The observations of Drs. Chen and Maddin on the change in the character of slip markings for a specific orientation might account, in part, for the differences found in the density of slip bands for crystals of different orientation. It would be interesting to know more details regarding the nature of the clustering; for example, if it is similar to that observed in  $\alpha$  brass crystals. On their basis, however, it is difficult to explain the similarity in density of slip bands (particularly for small strains) between crystals E and H, which have markedly different orientations. The character of the slip bands in these two crystals (as well as in crystal A) were quite similar; and, in contrast to crystal T, they appeared thicker and did display a minor tendency for dense clustering in some regions. Furthermore, in crystal T there was a greater evidence of the segmented type slip, reported and described in the paper as characteristic of deformation at lower temperatures. In view of the recent electron microscope studies of slip bands by Heidenreich and Shockley,<sup>31</sup> these observations do suggest that the amount of shear per slip band in crystals E, H, and G is greater than in T for a given amount of extension.

Recent experiments on single crystals of different metals at Sylvania Laboratories suggest a correlation between the nature of slip markings and changes observed in the shear hardening curve in regions of small plastic strain. These results also have emphasized a



definite need for more systematic and detailed studies of the nature of slip markings in single crystals possessing critical orientations.

**C. Crussard** (*Ecole des Mines, Paris, France*)—It is a very interesting fact that the aluminum crystals prepared by the authors by solidification display the same properties as the one I have made by recrystallization, regarding the discontinuous or steplike formation of slip bands.

The shape of the stress-strain curves observed by the authors on their crystals is also very similar to that of our recrystallized single crystals,<sup>32</sup> when only one glide system is active at the beginning. After 1 pct elongation, the new rise in our curves has been related by us to a strong increase in asterism and to the formation of deformation bands. It would be interesting to know if the same rise in the curve exists for the authors' crystals. In the case where two glide systems are active right from the beginning, we have observed a different shape of the stress-strain curve: It is parabolic from the beginning as has been postulated by G. I. Taylor; the asterism is stronger at the beginning than in the general case, but weaker at about 10 to 20 pct elongation, because no deformation bands are formed.

It is interesting to point out that the shape of stress-strain curves obtained by the authors on fused crystals seems in contradiction with the well-known experiments of Dehlinger and Gisen. The latter seems also in contradiction with some newer observations regarding the state of perfection of the crystals as shown by A. Guinier and myself.<sup>33</sup> Thus, it would be extremely interesting to have some X-ray information on the crystals used here by the authors, regarding the state of perfection of each of the subgrains of the lineage structure, for orientation (e.g. by Guinier's method) and intensity of reflection.

**F. D. Rosi**—Dr. Crussard's comments are both interesting and gratifying. It is significant to find that aluminum single crystals of similar purity produced by critical recrystallization show properties similar to those prepared by solidification from the melt. If structural irregularities are at the bottom of most plastic phenomena observed in real metals, then there can be no serious difference in the imperfections resulting from these two modes of single-crystal production of high purity metals.

With regard to a change in the shear hardening of these stress-strain diagrams, we also have observed a gradual rise in the curves at room temperature after an extension of about 0.4 pct. However, this value of extension appeared to vary with orientation, being somewhat less for those orientations nearer the [100] and [111] poles. At the temperature of liquid nitrogen this change of slope was not observed. Recent experiments on the extension of high purity silver single crystals (to be published) show a similar, but more marked inflection in the shear hardening curve after small amounts of extension (approximately 0.7 pct). Furthermore, a temperature dependence of this unique behavior has been fairly well established.

The extent of the X-ray studies was confined to ordinary back-reflection photograms, which were taken at various points along the circumference of the specimen. In general no asterism was observed up to extensions of approximately 1.5 pct for the room temperature tests. In view of the X-ray techniques used, no detailed study of structural imperfections in these crystals was possible. The only evidence of structural irregularities was the occasional presence of double diffraction spots indicative of the lineage imperfections. As mentioned in the paper, the angular spread

of these spots was never observed to exceed 2°.

It appears that the essential difference in the stress-strain diagrams reported by Dehlinger and Gisen on aluminum crystals prepared by solidification and those of the present investigation is in the sharpness of the yield point. In the case of the former, the yield point was ill-defined, which might very well be attributed to the lower purity of the metal, for, perhaps, the same reason that the yield point becomes less accentuated with decreasing temperature. Furthermore, it is quite possible that this same effect of increasing purity may be responsible for the rise in the stress-strain diagram after small extensions reported in the present investigation, but not observed by Dehlinger and Gisen in the less pure material.

**W. C. Ellis** (*Bell Telephone Laboratories, New York*)—Important new information for plastic behavior at several temperatures was reported in this paper for tests carried out with a nearly constant rate of stressing. Similar work has been done by other investigators using a constant strain rate. When a constant stress rate is used the strain rate is not necessarily constant over the range of a single test and usually is not. However, as shown in Fig. 5 of the paper, the strain rate is essentially constant in the plastic range for the individual tests. For tests at different temperatures, however, the strain rates are appreciably different, being substantially higher for the tests at 353°K. The importance of strain rate would seem to be that the recovery processes, being time dependent, are linked to the rate of straining—a faster rate permitting less recovery. Recovery in these tests would have been influenced not only by the different temperatures used, but also by the different strain rates. The latter may have been only minor although we do know that recovery proceeds (at least to some degree) in high purity aluminum at quite low temperatures. I should like to ask the authors to what extent they believe a varying strain rate may have affected the results and what the strain rates were in the tests?

**F. D. Rosi**—Dr. Ellis' question as to the effect of different strain rates at the different temperatures of testing on the results reported in this paper is indeed one worthy of consideration. It has been fairly well established that the speed of stressing has an insignificant effect at low temperatures and near the melting point, but a rather marked influence in an intermediate range of temperature. As Dr. Ellis points out, for aluminum of such high purity, this temperature range, where time effects are important, might very well be from room temperature to 200°C. Nevertheless, in view of previous investigations on the effect of strain rates on such fundamental properties as the critical shear stress and the coefficient of shear hardening, it appears very unlikely that this factor would affect these properties to an appreciable extent under the conditions of the present investigation, where the strain rate only varied by a factor of 5 over the temperature range of testing, see Table V. For example, in tests on aluminum at room temperature Weerts<sup>34</sup> found that on varying the speed of testing from 1:23,000 (450 pct elongation per sec) glide began at approximately the same stress, and the shear hardening increased by only 16 pct. In fact, even for hexagonal metals where this effect of varying strain rates appears to be more significant, a hundred-fold increase in the speed of testing is necessary to produce an increase in the critical shear stress of 20 to 30 pct. As corollary evidence, very recent experiments with high purity (99.99 pct) silver single crystals showed that a two-fold increase in the speed of stressing (for rates comparable to the experiments with aluminum) showed no change in the values for critical shear stress or coefficient of shear hardening.

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Table V. Variation of Strain Rate over Temperature Range Tested

| Testing Temperature, °K | Mean Strain Rate, Strain per Min |
|-------------------------|----------------------------------|
| 77                      | 8.2x10 <sup>-4</sup>             |
| 205                     | 4.1x10 <sup>-4</sup>             |
| 295                     | 2.7x10 <sup>-4</sup>             |
| 353                     | 1.7x10 <sup>-4</sup>             |



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## A Study of the Strain Markings in Aluminum

by Bani R. Banerjee

DISCUSSION, B. Averbach presiding

**R. G. Treuting** (Bell Telephone Laboratories, New York)—The author is first to be congratulated on a careful technique that has demonstrated the occurrence in aluminum at low temperatures of the strain markings observed in other face-centered cubic metals at normal temperatures, and the thermal instability of these markings.

In view of his findings, the author's hypothesis that either a stacking fault or an extended dislocation introduced by low temperature deformation has an associated energy higher than in other face-centered cubic metals is, as he says, logical, and worthy of some further comment:

1—The ratio of twin interface tension to grain boundary tension in aluminum has been found to be significantly higher than in copper.<sup>11</sup> To the extent that the respective grain boundary tensions are comparable, the twin interface tensions differ correspondingly. This would presumably apply in similar degree to twin faulting. Barrett<sup>12</sup> has also concluded from X-ray line width data that the faulting energy of aluminum is large.

2—R. D. Heidenreich<sup>13</sup> has found by electron microscopy that polygonization<sup>14</sup> of deformed aluminum occurs at the temperature of liquid nitrogen,  $-196^{\circ}\text{C}$ . Hence the recovery process proceeds at the temperature of the present experiments,  $-72^{\circ}\text{C}$ , probably at a significant rate.

3—There is evidence, e.g., Maddin, Mathewson, and Hibbard<sup>7</sup> that recrystallization twin bands are aligned with previous slip lines. This has been interpreted as indicating that slip generates twin faults in accordance with Mathewson's hypothesis. However, recent work by Burke<sup>15</sup> suggests strongly that twin faulting from slip cannot be the only source of twin bands observed in substantially recrystallized metals. The absence of twin bands in recrystallized aluminum may require further explanation than the thermal relief of twin faulting.

It would seem that a critical experiment is still needed to determine whether twin faulting is produced by slip. The method employed by Barrett<sup>16</sup> to establish stacking disorders in the Cu-Si system may profitably be applied to deformed metals, if a sufficient proportion of presumptively faulted planes can be generated without introducing so much lattice distortion as to obscure the X-ray data. This might be accomplished by a deformation mechanism permitting continuous or periodic shifting of the applied stress axis to maintain the pole of the latter within a single stereographic triangle of the single-crystal specimen projection.

The writer is indebted to his associates W. T. Read and R. D. Heidenreich for helpful discussions with respect to these comments.

**P. A. Jacquet** (Paris, France)—For the first time we succeeded in detecting "strain markings" far below the surface of a copper specimen which had been deformed by as small an amount as 1 pct in extension.<sup>17</sup> The observations of these markings is solely due to the sensitivity of the etchant. Thus with brass and other copper alloys a sodium hyposulphite electrolytic etch is far more sensitive than any other etch by known standard reagents.<sup>18</sup> With copper the most sensitive method is a short-cut etch into the electropolishing bath (phosphoric acid).

With aluminum bronze, some strain markings seem to correspond to microtwins, Fig. 6. With brass, the etch (Fig. 7) probably shows the regions where there are numerous whole sets of gliding lamellae which

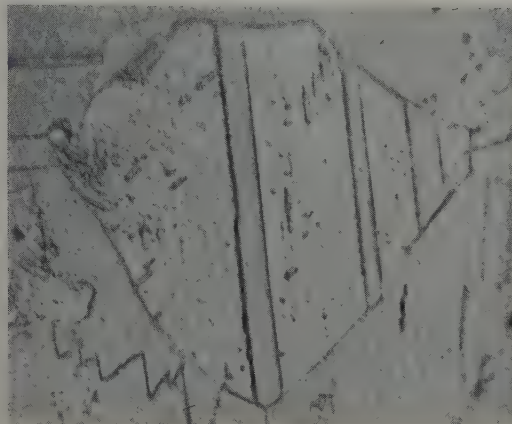


Fig. 6—Aluminum bronze annealed plate. X1600.

Surface abraded with emery paper No. 1. Electrolytic polishing to dissolve 15 micron thickness. Anodic etching in sodium hyposulphite at 0.4 pct. Strain markings show up as parallel striation systems oriented at  $60^{\circ}$ , on which a little element—which seems to be microtwins—can be seen.

form each slip line visible on the polished surface before etching.

The author stresses the importance of avoiding any heating for strain-marking observations, for instance mechanical polishing is performed by frequent coolings of the specimen down to  $-72^{\circ}\text{C}$ . But it is certain that during electropolishing a substantial superficial heating takes place, especially in the process described with No. 1 electrolyte where the current density is of the order 100A per sq decimeter.

Even with electrolyte No. 2 (described as  $\text{HClO}_4$ -acetic acid in the footnote, p. 1126, and  $\text{HClO}_4$ -acetic anhydride in Table I) an increase of the temperature exists. How does the author reconcile these two contradictory features?

**B. R. Banerjee** (author's reply)—The author is indebted to Dr. Treuting for his interesting comments, particularly for pointing out some recent experimental results tending to substantiate the author's hypothesis.

The author would also like to thank Dr. Jacquet for

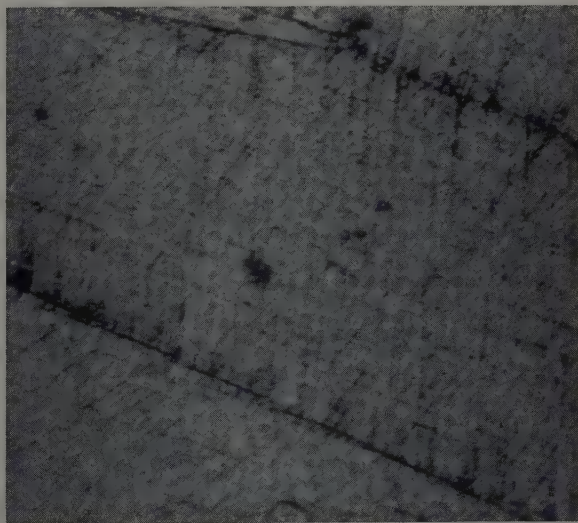


Fig. 7—Annealed  $\alpha$  brass. X1600.

Surface abraded with emery paper No. 2, then electropolished (dissolution 0.24 mm), final anodic etching in 0.1 pct sodium hyposulphite solution. The lower distinct diagonal line is a twin boundary.



his remarks. Although a small local heating undoubtedly does occur during electrolytic polishing, the constant contact with the cool electrolyte, and the short duration of polishing time, presumably help to keep the temperatures sufficiently low to prevent excessive recovery.

The author would like to correct the discrepancy pointed out by Dr. Jacquet. The electrolyte No. 2 was perchloric acid and glacial acetic acid.

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<sup>17</sup> P. A. Jacquet: *Comptes Rendus* (1944) **218**, p. 790; *Rev. Metallurgie* (1945) **42**, p. 133.

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## Activation Energy for Recrystallization in Rolled Copper

by B. F. Decker and D. Harker

DISCUSSION, R. Maddin presiding

**F. H. Wilson** (*American Brass Co., Waterbury, Conn.*)

—The authors are to be congratulated for employing a simple and direct technique for measuring the extent of recrystallization. By this method they are sure that they are determining the activation energy for recrystallization alone, uncomplicated by strain relief or other effects associated with recovery which hamper interpretations when the changes in other quantities during annealing are measured.

They tacitly assume that only the orientations which constitute the deformation texture and the "cubic" recrystallization texture are involved, and this assumption is related directly to the question of the origin of recrystallization textures concerning which opinions are still in conflict. It would be expected that their specimens showing maximum intensity from (200) planes reflections, having been rolled 98 pct, would have microstructures which show them to be 100 pct in the cubic orientation. Did they confirm this? Assuming this to be true, it would appear to be possible to employ the authors' data to determine whether the recrystallization texture resulted from "oriented nucleation" or from "oriented growth."

The value for the percentage of material transformed as derived from measurements of loss in intensity of (111) reflections would be independent of the orientations of the transformed material (except for the remote possibility that an appreciable number of the new nuclei would have [111] poles oriented the same as the deformation texture). However, the value as derived from measurements of gain in intensity of (200) reflections would depend upon whether the nuclei were all in the "cubic" orientation or whether other orientations formed. The values as derived from both sets of measurements would be equivalent throughout only if the nuclei formed in the "cubic" orientation. If values derived from (200) reflections are consistently lower at the start of recrystallization than those derived from (111) reflections, there would be some support for the theory of "oriented growth."

It would be of considerable value in contributing to our understanding of the mechanism of recrystallization if the authors could submit data to show the extent of agreement between the two sets of intensity measurements.

**M. Balicki** (*Polytechnic Institute of Brooklyn, Brooklyn, N. Y.*)—In 1937, A. Krupkowski and M. Balicki determined the activation energy for recrystallization of cold deformed copper<sup>5</sup> from both isothermal and isochronal experiments on cold-drawn commercial copper, using the change in mechanical properties as an index of structural changes. The values then obtained (32 and 31.5 kcal per mol) within the limit of accuracy, are identical with the figures obtained by the authors for OFHC copper (29.9 kcal per mol). M. Cook and T. L. Richards<sup>6</sup> in 1946 obtained values for the activation energy for copper of the order of 43 to 48 kcal per mol that are different from the values

found by the authors and in ref. 5 because of the employment of a different formula. It has been shown, however, that the isochronal annealing experiments performed by Cook and Richards yield values between 30.4 and 32.4 kcal per mol,<sup>7</sup> if treated by the method of Krupkowski and Balicki.<sup>8</sup> These figures compare well with the ones reported in the present paper for OFHC copper.

L. R. Jackson, A. M. Hall, and A. D. Schwoppe<sup>9</sup> used a value of 30 kcal per mol for the activation energy for the recrystallization of copper and the treatment of Krupkowski and Balicki to predict successfully the prolonged isothermal annealing behavior of various commercial grades of copper from the experimental data of short duration isochronal annealing.

The method adopted by the authors for heat treating isothermally is limited to relatively short times performed at relatively high temperatures, since changes in barometric pressure during prolonged treatments will affect the boiling points of the liquids used as an annealing medium and cause a fluctuation in the temperature. Did the authors perform their anneals at times when the barometric pressure was the same and did they note any deviations from the nominal annealing temperature by direct measurements? The quite feasible slight deviation from the nominal annealing temperatures would materially affect the location of the experimental points in Figs. 1, 2, and 4, so that the curves (with the exception of the last one in Fig. 4) might not give a true picture of the progress of re-annealing, and the two middle curves in Fig. 4 might be curved due to this cause.

Finally, the method is based on the assumption that during the recrystallization there is a change in orientation. As far as I know there is no proof that recrystallization will always bring about a different orientation from that of the cold deformed matrix. The accuracy of the method, therefore, will depend upon many factors which influence texture formation and will vary from case to case, such as: 1—Degree and character of impurity atoms present, 2—amount and character of alloy elements present, 3—the degree of cold work, 4—the mode of plastic deformation, 5—grain size and randomness produced by penultimate anneal, and 6—susceptibility to self-annealing during cold deformation and subsequent storage. Thus, a question arises about the accuracy of this new method and whether or not the degree of accuracy is the same for both types of copper tested. As a consequence, one is left wondering whether the differences in activation energy of 29.9 and 22.4 kcal per mol found by the authors are real or due to the systematic error of the method.

**B. F. Decker** (authors' reply)—Dr. Wilson's suggestion that knowledge of the agreement between measurements of the appearance of recrystallized material and the disappearance of cold-worked material would contribute to an understanding of the mechanism of recrystallization is well taken. The authors have not correlated data of this type for copper. However, Seymour and Harker<sup>6</sup> in their studies of 50 Fe 50 Ni alloy did



obtain both kinds of data. Their results are shown in Figs. 1 and 2 of their paper. For a given time and temperature there is good agreement between values obtained by the two methods for amount of material recrystallized. This would rule out the possibility that the texture sharpened by ordinary grain growth after recrystallization.

No microstructural investigation was made of the copper samples studied.

The authors thank Dr. Balicki for his interest in and comments on this paper, but they believe that his criticism of the accuracy of the method is not justified. All heat treatments in the boiling organic liquid at any one temperature were made on the same day, and temperature checks were made frequently with a calibrated thermometer. A temperature shift greater than  $0.5^\circ$  was never found and shifts of  $0.5^\circ$  only rarely. Consequently, the accuracy of the experimental points in Figs. 1, 2, and 4 is not affected materially by the method of annealing, and the shapes of the curves in Figs. 4 and 5 are real.

The authors admit that this method is not applicable to cases of recrystallization without change in orientation. However, primary recrystallization in copper is not such a case.

In reply to Dr. Balicki's suggestion that the difference in activation energy of 29.9 and 22.4 kcal per mol is due to error in the method, analysis of the data

shows that the maximum deviation of  $Q$  for the pure copper is 1.1 kcal per mol and for the OFHC copper 1.7 kcal per mol. Therefore, the maximum experimental uncertainty (2.8 kcal per mol) in the difference in activation energy for the two kinds of copper is very much less than the measured difference of 7.5 kcal per mol.

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## Recrystallization Reaction Kinetics and Texture Studies of a 50 Iron 50 Nickel Alloy

by William E. Seymour and David Harker

DISCUSSION, R. Maddin presiding

**A. A. Burr** (*Rensselaer Polytechnic Institute, Troy, N. Y.*)—I would like to say a few words about this interesting method of applying the X-ray spectrometer to measuring structural changes in metals. As the authors of both papers just presented\* have pointed out, the success of the method depends on the fact that: 1—The spectrometer when set up as described, measures diffracted energy only from planes parallel to the face of the specimen. 2—A high degree of preferred orientation exists in the specimen initially and a change in grain orientation occurs as the process under study proceeds.

I would like to point out another metallurgical problem where the same principles have been utilized. In some work done in 1943 at the Pennsylvania State Col-

lege<sup>9</sup> involving the interdiffusion of thin films of copper and zinc, an analogous setup was used to follow the diffusion process and to verify the Widmanstätten relationships between the phases in this system. In this case the zinc film exhibited a high degree of preferred orientation with the basal planes parallel to the glass substrate. As the structure changed with diffusion at relatively low temperatures the breakdown of the zinc structure and the growth of that of  $\beta$  brass could be followed. From the preferred orientation of the resultant brass the Widmanstätten orientation relationships could be determined.

**W. E. Seymour and D. Harker** (authors' reply)—We are very grateful to have been reminded by Professor Burr of the work done by him and others at Pennsylvania State College, using X-ray diffraction methods similar to ours; our failure to give reference to this work was due entirely to oversight.

\* This refers to paper by B. F. Decker and D. Harker, the discussion of which is on p. 548, this volume, and this paper.

<sup>9</sup> Burr, Coleman, and Davey: An X-Ray Study of Brasses Formed by the Interdiffusion of Copper and Zinc Deposited on Glass by Vaporization. *Trans. ASM* (1944) **33**, p. 73.

## The Textures of Cold-Rolled and Annealed Titanium

by Howard T. Clark, Jr.

DISCUSSION, R. Maddin presiding

**M. K. Yen and J. P. Nielsen** (*New York University, New York*)—We wish to compliment Dr. Clark on his excellent work and interesting results. The double texture reported in this paper was found to be in good agreement with our results on iodide titanium after 97.75 pct reduction by cold rolling.<sup>8</sup> The rolling texture was characterized by a clustering of the (0001) poles around two axes lying in the transverse plane and inclined at  $30^\circ$  to the rolling plane. The average grain orientation for the specimen could be shown schematically as in Fig. 4. Moreover, this double texture also was found in iodide titanium deformed by compression. The usual [0001] compression texture occurring in h.c.p. metals was observed for reductions up to about 85 pct. However, a pronounced double texture comparable to that shown in Fig. 1c of Dr. Clark's paper was obtained

when a specimen was subjected to compression rolling totaling about 94.5 pct. The difference in preferredness between the center and the surface material in compression rolled specimens also was studied. The results

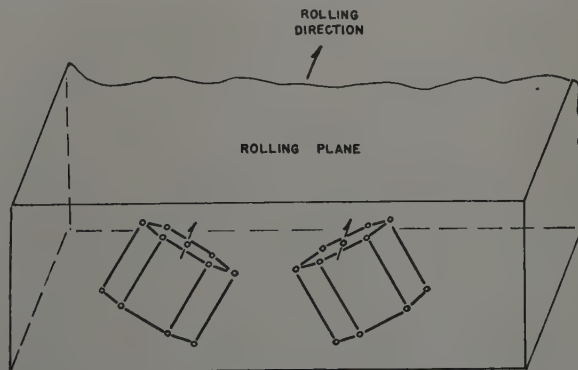


Fig. 4—Schematic diagram of average grain orientations of  $\alpha$  titanium after a reduction of 97.75 pct by cold rolling.

Table II. Types of Pole Figures for Various Rolled Close Packed Hexagonal Metals

| Metals | C:A Ratio | Type of Scattering                                           | Reference                                                    |
|--------|-----------|--------------------------------------------------------------|--------------------------------------------------------------|
| Zn     | 1.856     | 20°-25° toward rolling direction                             | Caglioti and Sachs <sup>9</sup>                              |
| Cd     | 1.885     |                                                              | Valouch <sup>10</sup>                                        |
| Mg     | 1.624     | i. Equal scattering<br>ii. Slightly toward rolling direction | Schmid and Wassermann <sup>11</sup><br>Bakarian <sup>2</sup> |
| Zr     | 1.590     | Scattering toward transverse direction                       | Burgers and Jacobs <sup>1</sup>                              |
| Ti     | 1.587     |                                                              | Clark, <sup>12</sup> Yen <sup>8</sup>                        |
| Be     | 1.568     |                                                              | Smigelskas and Barrett <sup>3</sup>                          |

obtained were similar to those of Dr. Clark on straight rolling, i.e., the center material had a more pronounced double texture than did the surface material.

In the case of wires by rolling for 85 pct reduction in area, the following planes were found to lie perpendicular to the wire axis, in the order of prevalence: (1010), (1011), and (0001). A relatively sharp [1010] texture was observed in a wire specimen reduced 92 pct in area.

If we make a correlation of the type of distribution of the basal planes in the pole figure with *c:a* ratio, as in Table II, we find that the first group, Zn and Cd (*c:a* > 1.633), has a scattering toward rolling direction and that the third group, Zr, Ti, and Be (*c:a* < 1.633) has a scattering toward transverse direction. In the case of Mg, the *c:a* ratio is quite close to 1.633, and it exhibits both directions of scattering although a scattering tendency has been reported similar to that of

the Zn and Cd group. The variations in the reported Mg results may be accounted for by slight changes of *c:a* ratio around the ideal 1.633 value due to the presence of impurities.

The scattering in the rolling textures of the metals listed in Table II may be related to twinning as well as to the *c:a* ratio. For Zn and Cd, twinning results in elongation along the twinning direction and for Zr, Ti and Be, twinning produces a shortening in the twinning direction. For the first group the flow of metal would be assisted by twinning along the rolling direction and thus twinning might be related to the scattering toward the rolling direction. Dr. Clark has pointed out that twinning on the (1102) planes of Ti would yield a thickening of the metal. However, since twinning in Zr, Ti, and Be produces a shortening which is inconsistent with the flow of the metal, its relative occurrence would be greater in the transverse direction than in the rolling direction. This type of twinning then would be related to the observed scattering toward the transverse direction.

It is also interesting to note that at certain orientation at which the twinning plane in h.c.p. metals is parallel to the rolling plane, e.g., the basal plane of Ti makes an angle of 42°30' with the rolling plane, twinning may occur with no change in thickness of the metal.

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## Production and Examination of Zinc Single Crystals

by D. C. Jillson

DISCUSSION, R. Maddin presiding

**A. J. Goss and S. Weintraub** (*University College, Southampton, England*)—We have read Dr. Jillson's paper with considerable interest, particularly as we consider any detailed information with regard to the growth of metal crystals of extreme importance. Recently we have carried out a similar comprehensive investigation of the influence of temperature gradient and rate of growth on the successful production of single crystals of tin. A brief report of the results obtained will appear shortly in *Nature*. Andrade and Roscoe's method<sup>12</sup> with a horizontal traveling furnace was used, and the crystals were grown from the melt, in vacuo, in pyrex glass tubes. More recently we have turned our attention to zinc, and the results of our preliminary experiments on 99.95 pct purity Zn may be of interest. Each specimen of zinc before crystallization was in the form of a cast rod 25 cm long and 5 mm diam and was contained within an open pyrex glass tube of approximately 7 mm internal bore. The specimen and its surrounding glass tube was placed inside the furnace tube where a vacuum of the order of 10<sup>-2</sup> mm Hg was maintained, during the process of crystallization. Various speeds of growth and temperature gradients were tried. The yield of good single crystals was 13 out of 15 specimens, 3 out of 11, and 0 out of 9, for 0.5, 1.5, and 5.3 mm per min speeds of growth, respectively. In the imperfect specimens the structure usually consisted of several parallel separate crystals along the length of the rod. It should be noted that the slowest speed used, namely 0.5 mm per min is slightly greater than that corresponding to 8°C per in. and 7.4°C per hr for which Dr. Jillson obtained 100 pct yield.

It is stated by Dr. Jillson that preferred directions of crystal growth in zinc crystals may be influenced by very small amounts of impurities. For 99.99+ pct pure Zn he found a preference for the basal planes to be within 20° of the perpendicular to the specimen

axis; but for 99.999+ pct pure Zn, they were randomly orientated. We have found that for 99.95 pct Zn there is a marked preference for the angle between the *c*-axis, [001], of the successfully grown crystal and the specimen axis to be 70° to 90°. From suitable test temperature measurements that we have taken, it would appear that the direction of heat flow is along the specimen axis. It would be desirable to test further whether impurities are a controlling factor on the orientation, and we are extending our experiments to purer zinc.

The opinion has been expressed by those who have used methods for the production of metal single crystals in which the metal is held vertically, that the pressure of the superincumbent metal does not affect the crystal growth. However, we believe that this is still a matter of some doubt and would question whether, in addition to the proper direction of heat flow and impurity content, the presence of some 20 in. of superincumbent metal as in Dr. Jillson's case is not also a determining factor affecting the growth and possible orientation of the single crystal.

For the determination of the orientations of our zinc single crystals, we use the optical reflection method described by Chalmers,<sup>13</sup> and we have found that the thermal etching due to the normal vaporization of the crystal gives sharper reflection patterns than any of the chemical etchants mentioned by Dr. Jillson. We would recommend the use of the thermal etching. Nevertheless we do regard Dr. Jillson's results obtained by chemically etching the surface as of considerable interest and importance.

We would be glad to have more detailed data of the various speeds of growth and temperature gradients used by Dr. Jillson so as to check whether there is any relation between these two quantities and the yield of single crystals.

**E. S. Greiner** (*Bell Telephone Laboratories, New York*)—Crystal imperfections such as lineage result in



increasing the angular spread of back-reflection Laue spots. Since the ridges on the surface of the crystal shown in Fig. 5 of the paper may be evidence of lineage in the zinc, I wish to ask the author if he observed any significant difference in the angular spread of back-reflection spots depending on whether the X-rays were reflected from a ridged or a smooth area of the surface. Was there any change in the angular spread of corresponding Laue spots reflected from various areas of the crystal surfaces? This information would aid in evaluating the perfection of these zinc crystals.

**G. Edmunds** (*American Brake Shoe Co., Mahwah, N. J.*)—The author has observed a wide range of orientations of the single crystals produced from 99.999 + pct Zn and has suggested "a possibility that preferred directions of crystal growth in zinc crystals may be influenced by very small amounts of impurities." What seems to be a more likely explanation of the occurrence of random orientations is that the perfection of Dr. Jillson's experimental technique, together with the small content of impurities that might nucleate growth, has resulted in only one nucleus being a center of crystallization. Except insofar as nuclei might tend to be oriented preferentially, this should lead to randomness of crystal orientation. Under less perfect experimental conditions more centers of crystallization would be expected, and there would be a tendency for those crystals to survive and extend whose [210] direction (nearly<sup>14</sup> the direction of maximum growth rate) most nearly paralleled the direction of the maximum thermal gradient. Thus, it seems logical to expect more randomness of orientation in exceptionally pure metal, but not an influence on the preferred direction of crystal growth as suggested by Dr. Jillson.

**D. C. Jillson** (author's reply)—The data of Goss and Weintraub suggest better yields at lower growth rates, but do not show the separate effects of temperature

gradient and cooling rate. A high cooling rate and temperature gradient can give the same growth rate as a low rate and gradient, but might give different results. We have not run enough tests with high or low temperature gradients or at high cooling rates to draw conclusions as to relative probabilities of success. We believe that success depends largely upon control of nucleation and that purity is a very important factor. With higher purity, the range of conditions for successful growth may be wider.

The data of Goss and Weintraub on orientation preferences in specimens of lower purity seem to support our own very meager data suggesting a possible influence of impurities on preferred direction of crystal growth. The arguments of Mr. Edmunds against this are very logical, but might be qualified to read "there would be a tendency for those crystals to survive and extend which have a direction of maximum growth rate (nearly [210] in zinc of 99.99 + pct purity or less) most nearly parallel to the direction of the maximum thermal gradient." Lacking definite data on growth rates in different directions in zinc of higher purity, and considering the present data and other data more recently brought to our attention, we feel that the question might be kept open.

We are sorry that we cannot answer Dr. Greiner's question regarding the angular spread of back-reflection spots from the ridged areas, because we prepared no back-reflection patterns of these areas. They were relatively lead-rich areas and we attributed the ridges to lead segregation.

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## The Structure of Intermediate Phases in Alloys of Titanium with Iron, Cobalt, And Nickel

by P. Duwez and J. L. Taylor

DISCUSSION, B. D. Cullity presiding

**E. S. Greiner** (*Bell Telephone Laboratories, New York*)—In order to reveal the presence of ordering in alloy systems by the X-ray technique, the superlattice reflections must be of sufficient intensity for detection. If the scattering powers of the elements in the alloy are quite different, e.g., Cu-Au or Fe-Si, the reflections from the superlattice are intense and can be detected by usual X-ray procedures. If, however, the alloys are composed of elements whose atomic numbers differ by one or two, e.g., Cu-Zn, Fe-Co, or Fe-Ni, the superlattice reflections are very weak because of the small differences of scattering powers. In these cases it is necessary to select the radiation so as to obtain differences in scattering powers of the elements in the

alloy, which are sufficient for the production of superlattice reflections. The method of selection has been described in the literature.<sup>10</sup>

The present paper describes X-ray tests which did not reveal ordering in Ti-Fe, Ti-Co, and Ti-Ni alloys, the atomic numbers of whose elements differ by 4, 5, and 6, respectively. I wish to ask the authors if one must select a favorable radiation to be certain of the detection of order, if present, in alloys such as these.

**P. Duwez and J. L. Taylor** (authors' reply)—It is true that by means of a proper choice of radiation it is possible to increase the difference between the scattering factors of two atoms in a crystal. This method, however, has not been used in the present investigation. It is therefore possible that very weak reflections were not detected on the X-ray diffraction patterns and more careful measurements might reveal the existence of an ordered structure in the TiFe, TiCo, and TiNi phases.

<sup>10</sup> A. J. Bradley and J. W. Rodgers: *Proc. Royal Soc.* (1934) **144A**, p. 340; and F. W. Jones and C. Sykes: *Proc. Royal Soc.* (1937) **161A**, p. 440.

## On the Martensitic Transformation at Temperatures Approaching Absolute Zero

by S. A. Kulin and Morris Cohen

DISCUSSION, A. R. Troiano presiding

**J. C. Fisher, J. H. Hollomon, and D. Turnbull** (*General Electric Co., Schenectady*)—The authors have done an excellent piece of work in demonstrating that martensite plates form rapidly in stainless steel at a temperature of 4°K. According to the relationship:

$$\text{Rate} = v \exp(-Q/RT) \quad [1]$$

an appreciable growth rate at 4°K corresponds to an activation energy  $Q$  of 100 cal per mol or so at the most. Using this argument, they have suggested that the atom-by-atom growth mechanism proposed for

martensite probably is incorrect, and that a growth mechanism analogous to the propagation of sound waves is more likely.

The authors' observations are not in agreement with those of Kurdjumov and Maksimova, who report an activation energy  $Q_m = 1600$  cal per mol for the growth of martensite in 0.6 pct C, 6 pct Mn steel, and near cessation of the martensite transformation below -200°C in this alloy. However, it may be possible to reconcile the two sets of observations.

The zero-point energy of a mol of crystalline solid is  $E_0 = (9/8) R\theta_D$ , according to the Debye model, where  $\theta_D$  is a constant in the neighborhood of 10°.



This energy is split up among modes of vibration having energies varying from nearly zero to about  $(3/2) R\theta_D$  cal per mol, raising a question as to the validity of eq 1 except for values of  $Q > (3/2) R\theta_D$ . For iron,  $\theta_D = 420^\circ\text{K}$ ,  $E_0 = 950$  cal per mol, and  $(3/2) R\theta_D = 1260$  cal per mol. Hence, whenever  $Q$  is in the neighborhood of 1000 cal per mol in iron, the zero-point energy may be sufficient to allow the process to continue at  $0^\circ\text{K}$  by the tunnel effect.

If the activation energy  $Q_m$  for the unit process of the martensite transformation, thought of as an atom-by-atom process, is a function of composition, it may be possible to vary  $Q_m$  from a relatively large value where eq 1 is valid and Kurdjumov and Maksimova's observations could have been made, to a somewhat smaller value, less than the zero-point energy, where eq 1 may be invalid and the growth process could take on more of the characteristics of sound-wave propagation.

In order to check this hypothesis, it is necessary, among other things, to repeat the work of Kurdjumov and Maksimova, whose observations have not been reproduced yet despite earnest attempts by the authors. Although it is possible that Kurdjumov and Maksimova were mistaken in their observations, it is more probable that their published alloy compositions are in error, or that a misunderstanding of some sort exists concerning their procedure. These possibilities are being examined in a series of experiments being undertaken in our laboratory.

**C. Crussard** (*Ecole des Mines, Paris, France*)—The fact that martensite is formed at temperatures as low as  $4^\circ\text{K}$  is extremely interesting in itself; but in its interpretation there is need for care. At first glance, it seems to substantiate the theory of athermal nucleation of martensite, as no activation seems possible at absolute zero. But this conclusion is incorrect, because the theory of thermal motion generally accepted for solids is incorrect. I have shown elsewhere<sup>17</sup> that for transformation involving a simultaneous displacement of several atoms, the Boltzmann formula does not apply; the correct theory must take in account the interferences of thermal waves. A rough hypothesis has led me first to a formula of the type:

$$P \approx e^{-\sqrt{A/\epsilon}} \quad [2]$$

where  $P$  is the probability of activation,  $A$  an energy involving the shape of the nucleus, and  $\epsilon$  the expression of the energy for a mode of vibration:

$$\epsilon = h\nu \frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1} \quad [3]$$

The active frequency,  $\nu$ , depends also on the size of the nucleus; it is never far from the cutoff frequency.

A better, but still approximate calculation (to be published) leads to a more satisfying formula:

$$P \approx e^{-\frac{A}{\epsilon}} \quad [4]$$

The formula holds also for single atoms.

Thus, activation is possible even at absolute zero (another possibility being the "tunnel effect" for electrons). The departure between the Boltzmann formula and the eq 4 is very difficult to test by experiment. Martensite transformation seems the best example. The author's experiments can be explained by eq 4, if it is assumed that martensite nucleates at quenching temperature.

The athermal nucleation theory, assuming martensite embryos to be formed at austenitizing temperature, actually meets very great difficulties:

1—If it is assumed that the embryos are produced by local fluctuations in composition of the alloy, the size-distribution curve of embryos is independent of temperature; thus stabilization of austenite cannot be explained. Moreover, the reverse transformation cannot be explained easily.

2—If it is assumed that the embryo is of the dislocation type, all the experimental facts do rather prove that dislocations stabilize austenite: On the other hand,  $M_s$  should strongly depend on the state of polygonization of austenite, a fact which has not yet been observed, to my knowledge.

It seems easier to explain stabilization of austenite by some kind of hardening in the austenite itself (some new experiments in my laboratory point to that result), which increases the stress-energy barrier to the transformation, because martensite cannot be formed without some kind of plastic deformation in the platelet or in the surroundings. Thus, there is no reason to reject the theory by which martensite is formed at quenching temperature, as is assumed by Scheil and others, according to the detailed mechanism of grouping of thermal waves which I proposed.<sup>18</sup>

**N. A. Ziegler and P. H. Brace** (*Crane Co., Chicago*)—This very interesting paper, and particularly that part of it which deals with subzero transformations in 18-8 type steels, illustrates and rationalizes some of our observations.<sup>19</sup>

One of the present discussers as early as February 1947 discovered that Charpy bars, made of certain austenitic stainless steel compositions, after having been fractured at the temperature of liquid nitrogen (about  $-300^\circ\text{F}$  or  $-185^\circ\text{C}$ ), became, adjacent to the fracture, rather strongly magnetic. This increased magnetic permeability persisted at room temperature and apparently was caused by an (at least partial) transformation of the austenitic phase into ferritic.

This supposition was substantiated by hardness measurements taken close to the fracture ("magnetic" region), as compared to those taken away from the fracture ("nonmagnetic" region). The "near-fracture" hardness, at least in some cases, increased to values seldom observed in conventionally cold-worked steels of this type. Likewise, microexamination of "near fracture" regions disclosed structures very similar to that shown by the authors' Fig. 2b. None of these phenomena could be observed in the bars of similar compositions, but fractured at room temperature. Nor could they be produced in samples plastically deformed at room temperature and then cooled to the temperature of liquid nitrogen.

Briefly, it was demonstrated that this  $\gamma$  to  $\alpha$  transformation was promoted by a simultaneous application of plastic deformation and low temperature and could not be produced by these two factors applied separately.

Subsequent and more elaborate experiments established that compositional range, in the family of Fe-Cr-Ni alloys, which responds to the mechanical working at subzero temperatures. Roughly, it can be defined on the triaxial diagram by the following points: 18 pct Cr-4 pct Ni, 12 pct Cr-20 pct Ni, and 30 pct Cr-14 pct Ni.

However, in order to develop this effect to its maximum, these steels have to be thus worked to about 70 pct reduction of the original cross-sectional area. This was demonstrated by rolling and wire-drawing experiments, each performed in several consecutive steps of simultaneous chilling and plastic deformation. Even though this hardening effect can be achieved at temperatures as high as  $-100^\circ\text{F}$  ( $-73^\circ\text{C}$ ), for practical reasons chilling in liquid nitrogen was found to be more convenient.

Moreover, it also was found that such steels, plastically deformed at a subzero temperature, can be made still harder by aging them at about  $750^\circ\text{F}$  ( $400^\circ\text{C}$ ).

Other physical properties are affected in the same proportion as hardness, so that in an 18-8 strip rolled at  $-300^\circ\text{F}$  ( $-185^\circ\text{C}$ ) and aged at  $750^\circ\text{F}$  ( $400^\circ\text{C}$ ) the following values can be obtained: tensile strength, 295,000 psi; yield stress, 290,000 psi; proportional limit, 264,000 psi; elongation, 2.0 pct; reduction of area, 24.8 pct; and hardness, 607 V.P.N. More recently, hardness values of well over 700 V.P.N. have been obtained.



Some preliminary experiments have shown the possibility of a considerable improvement in the wear resistance of austenitic Cr-Ni steels. Likewise, some exploratory tests indicate that the salt-water corrosion resistance of samples thus treated is not greatly affected by the special hardening process described.

In a word, it appears that the phenomenon of martensite formation in austenitic stainless steels, so ably described by Kulin and Cohen, might have valuable practical applications.

**S. A. Kulin and M. Cohen** (authors' reply)—The discussion submitted by Drs. Fisher, Hollomon, and Turnbull is most ingenious, and warrants careful consideration because it points up the very issue that this paper seeks to settle. Of course, it is true that the Boltzmann equation may lead to serious discrepancies at temperatures approaching absolute zero. However, we used the equation only because it is a consequence of the atom-by-atom mechanism of growth which the discussers have postulated, and we wished to test the predictions of this mechanism in a critical way.

In the light of the present paper, Drs. Fisher, Hollomon, and Turnbull suggest that the Boltzmann equation may still be applicable to the martensite transformation for alloys in which the activation energy for growth is larger than the zero-point energy of the lattice ( $\sim 1000$  cal per mol), a possible example being the 0.6 pct C, 6 pct Mn steel of Kurdjumov and Maksimova who reported an activation energy of 1600 cal per mol. However, in the case of the alloys studied in the present investigation, the discussers propose that the activation energy may be less than the zero-point energy and hence the growth may "take on more of the characteristics of sound-wave propagation."

The above distinction appears questionable in view of the following. A 0.6 pct C, 8 pct Mn steel was strained at 4°K, and the martensite content increased from about 90 pct (the amount formed on straight cooling) to about 99 pct during the brief straining period. If the available 10 pct austenite were retained because of a slow atom-by-atom diffusion process, it could not be induced to transform appreciably at 4°K within the few seconds of straining. Furthermore, Kurdjumov and Maksimova<sup>20</sup> have recently reported an activation energy of only 600 cal per mol for a ferrous alloy of 23 pct Ni, 3.4 pct Mn. Notwithstanding this low activation energy, the indications are that the transformation characteristics at low temperatures are quite similar to those of the 0.6 pct C, 6 pct Mn alloy.

These findings indicate that there is considerable doubt concerning the significance of the 1600 and 600 cal per mol values as activation energies for martensitic growth. Other interpretations are possible; for example, Kurdjumov and Maksimova regard these values as the activation energies for nucleation. Thus, the reaction may be controlled by the availability of

nuclei rather than by the rate of atomic diffusion. This question will be dealt with by E. S. Machlin in a forthcoming paper on isothermal martensite formation.

Professor Crussard points out some of the difficulties in the athermal embryo theory of martensite nucleation and presents arguments in favor of isothermal nucleation due to the grouping of thermal waves. Actually there is now strong experimental evidence contrary to both of these viewpoints and in favor of the strain embryo concept. The case against isothermal nucleation resulting from thermal fluctuations or waves is indicated by the following experiment conducted by E. S. Machlin. If the isothermal transformation in a 70 pct Fe, 30 pct Ni alloy at  $-70^{\circ}\text{C}$  is interrupted by heating briefly to about  $60^{\circ}\text{C}$ , the subsequent transformation at  $-70^{\circ}\text{C}$  is almost completely inhibited. On the other hand, if the holding at  $60^{\circ}\text{C}$  is conducted before the first cooling to  $-70^{\circ}\text{C}$ , there is no effect on the isothermal transformation at  $-70^{\circ}\text{C}$ . In both instances, the thermal fluctuations or waves at  $-70^{\circ}\text{C}$  are the same, but the isothermal reaction depends on the state of strain due to the martensite formed on cooling. If relaxation is allowed to take place, the isothermal transformation is reduced in magnitude. In other words, the nucleation of isothermal martensite does not result from thermal vibrations alone, but from their superimposition upon existing strains which are produced, for the most part, by the martensite formed during cooling.

Recent experiments on the effect of plastic deformation substantiate the strain embryo theory of martensite nucleation. Plastic deformation of single crystals raises  $M_s$ , and slip lines do not stabilize the austenite. The same tendency exists in polycrystalline alloys, but the effect may be obscured because the nonhomogeneous deformation partitions the austenite and causes the martensite to form in smaller units.

The remarkable strengthening of austenitic stainless steel by deformation at subzero temperatures, as described by Drs. Brace and Ziegler, is a striking application of the principles of martensite formation. This unusual type of metal processing has commercial potentialities and its effective utilization will be watched with interest.

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- <sup>20</sup> Kurdjumov and Maksimova: *On the Energy of Formation of Martensite Nuclei*. *Doklady. Akad. Nauk. USSR* (1950) **73**, No. 1, p. 95. Brucher Translation No. 2565.

## The Isothermal Transformation of a Eutectoid Beryllium Bronze

by Ronald H. Fillnow and David J. Mack

### DISCUSSION, A. R. Troiano presiding

**R. Haynes** (*University of Sheffield, Sheffield, England*)—The authors have presented some interesting data on the isothermal transformations of 6 pct Be-Cu. The reactions are extremely interesting for they appear to show a type of reaction which has not been noted before. The previously accepted temperature of the eutectoid is surprising in view of the relatively rapid rates of transformation observed in these experiments.

The growth of coarse eutectoid from fine eutectoid is an unusual phenomena, since on quenching to room temperature the phases present before and after the reaction appear to be the same. This reaction is attributed to recrystallization of  $\alpha$ . Recrystallization usually is associated with the release of strain energy from a deformed lattice. It seems to be unlikely that sufficient strain will be imparted to the lattices of the

products of transformation at the high temperatures to provide sufficient energy for a recrystallization process, neither will sufficient energy result from the decrease in interfacial area between the two phases. One would expect that strains will be dissipated almost as soon as they are set up due to the plastic condition of the metal at the high temperature. It is difficult to conceive the recrystallization of one phase affecting the distribution of a second phase with which it is associated.

Consider the formation of a lamellar eutectoid from a solid solution. The conditions may be represented by Fig. 34, the lamellae lying in a direction at right angles to the plane of the paper. The growth of such an aggregate is edgewise, as is expected from theoretical considerations.<sup>10</sup> If we assume that the shaded lamellae are representing the  $\gamma$  phase in copper beryllium and the unshaded the  $\alpha$  phase, which are growing through the  $\beta$



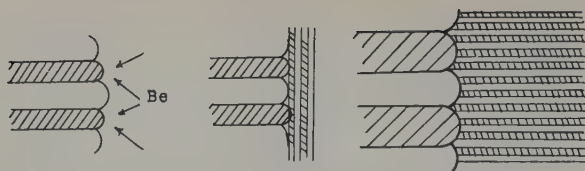


Fig. 34 (left)—Mechanism of growth of eutectoid lamellae.

Figs. 35 (center) and 36 (right)—Hypothetical mechanisms of growth of eutectoid lamellae from finer eutectoid lamellae.

phase, then immediately in front of the advancing lamellae, the beryllium atoms in the  $\beta$  phase would be expected to diffuse towards the  $\gamma$  plates, while copper atoms will tend to diffuse towards the  $\alpha$  plates. Consider now the growth of coarse lamellae of  $\alpha$  and  $\gamma$  through finer lamellae of  $\alpha$  and  $\gamma$ . The conditions are as shown in Figs. 35 and 36. For the coarse lamellae in Fig. 35 to grow, it is necessary that diffusion should occur in the thin lamella of  $\gamma$  phase, or  $\alpha$  phase, as the case may be. This implies that in part of the  $\gamma$  lamella some of the beryllium content must diffuse away until formation of the  $\alpha$  phase occurs, or in the case of an  $\alpha$  lamella, the beryllium content must be increased by diffusion until  $\gamma$  phase is formed in certain areas. Similar difficulties are met in the case of Fig. 36, since diffusion, as indicated, would result in the alloy going from a more stable to a less stable condition. This is contrary to thermodynamics and to previous observations. It might well be asked, where does the constraint which initiates such diffusion come from? On this assumption it may be expected that coarse eutectoid will grow through coarse eutectoid, yet this is not observed. It is suggested, therefore, that at the temperature of reaction the fine eutectoid structure observed is not composed of the  $\alpha$  and  $\gamma$  phases but of some intermediate phase, or phases, which break down to  $\alpha$  and  $\gamma$  during quenching. Such a phase could give a coarse structure isothermally, while not precluding the possibility of the  $\beta$  phase breaking down directly into the coarse structure. One wonders if there is more in the lamellar appearance of the  $\beta$  phase noted at 500°C than has been assumed. By analogy one is reminded of the formation of eutectoid from both  $\beta$  and  $\beta_1$  in eutectoid copper aluminum, although the analogy should be treated with caution. Thus two paths seem to be possible for the decomposition, i.e.  $\beta$  to fine eutectoid to coarse eutectoid, and  $\beta$  to coarse eutectoid. It would be interesting to know if after quenching to room temperature the fine eutectoid will continue to form coarse eutectoid when replaced in the isothermal bath.

Klier and Grymko<sup>3</sup> indicated in their paper that the interlamellar spacing of the eutectoid aluminum bronze behaved in an anomalous manner: First decreasing and then increasing as the transformation temperature was lowered. This has been confirmed in a quantitative

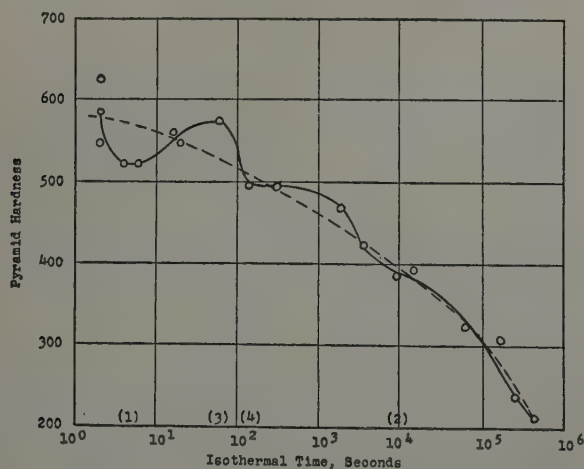


Fig. 37 (right)—Authors' Fig. 19 plus additional data.

manner. Do the interlamellar spacings of the fine and coarse eutectoids show a similar behavior?

It would be interesting to learn if any relationship exists between the lamellae of the fine and coarse eutectoids.

It has been observed in eutectoid copper aluminum alloy isothermally transformed to eutectoid below the  $M_s$  temperature that pseudomorphs of the martensitic structure can be seen, so that pseudomorphs of the fine eutectoid in the coarse eutectoid do not seem to be evidence for the phases present in the fine eutectoid being  $\alpha$  and  $\gamma$ .

At the lower temperatures it has been observed that a metastable precipitate forms early in the reaction and then quickly disappears and is followed by the "ripple" structure. The product of such a reaction cannot be  $\beta$ . Would it not be better to designate it by  $\beta'$  or some other symbol? The ripple structure then takes on a mottled appearance. This is similar in appearance to the latter stage of the  $\beta$  to  $\beta_1$  reaction in eutectoid copper aluminum. May not the reaction be analogous?

There seems to be little justification for the use of two hardness scales on the hardness-transformation-time diagrams. Even in a single phase alloy the results are not directly comparable. On a multiphase alloy one wonders if any simple correlation can exist. The use of microhardness for following isothermal reactions seems to be open to question. Such a method must result in the hardness of only one of the many constituents being determined by any one impression, with the result that for a number of impressions which are randomly distributed the hardness of a partially transformed specimen will vary over a very wide range. This difficulty can be overcome by the use of a large indenter, say a 10 mm Brinell ball: This is not possible if small specimens are to be used, or by taking numerous hardness impressions and computing a mean value. The claim that the microhardness data correlates well with observed microstructures seems rather sweeping. In Fig. 30, for example, the results appear to show a scatter of 100 points pyramid for a structure which does not change greatly with time. Fig. 19 shows a number of undulations in the curve. On examination of the curve it might be concluded that points (3) and (4) (my reference marks in Fig. 37) were of significance. This is not so. It is possible to draw a fairly smooth curve, as shown, for the results from 500°C downwards. This, however, results in the elimination of the "significant" change in direction at (2). To a lesser extent this criticism can be levelled at most of the hardness curves. One concludes that the use of microhardness, by itself, is completely unsuitable for following the reactions, and that the various "start" and "finish" times on the curves are derived from microscopical evidence.

Confirmation of the microscopical results is made by the X-ray diffraction method. By examination of the photographs in the cases of coarse and fine eutectoid, it can be seen that at high angles of reflection the doublet  $\alpha$  of the  $K_\alpha$  radiation appears to be resolved, while in the case of the slowly cooled alloy the ring is blurred. In a quenched alloy the rings are expected to be blurred and the doublets unresolved at high angles. This is borne out by quenched specimens of the eutectoid Cu-Al alloy. One is led to wonder how efficient was the quench, or if the specimens have received a stress relieving anneal? If so, it is not possible that changes may have occurred.

**J. E. DeMoss** (University of Notre Dame, Notre Dame, Ind.)—I have been working on the transformations of the  $\beta$  phase in the Be-Cu system for some time and, hence, particularly appreciate the peculiarities and complexities which confronted the authors.

From my results, I agree with the authors that the accepted eutectoid horizontal temperature is too low and that actually it is somewhat above 600°C. This has been pointed out by Thomas.<sup>11</sup>

My results on the isothermal transformation of a eutectoid Be-Cu alloy are in essential agreement with those of the authors. I have observed many of the



"unusual microstructures" which have been shown in this paper including the initial appearance of fine pearlite and its ultimate replacement by coarse pearlite. However, I find it difficult to accept that the coarse pearlite forms from the fine pearlite by a nucleation and growth process, although that may appear to be the mechanism.

Evidently the  $\beta$  grain size of the authors' alloy must have been reasonably small. I have observed that the time for completion of the isothermal reaction is quite long, even at 500°C, when the  $\beta$  grain size is of the order of 1.5 mm average grain diameter. The time for the beginning of the reaction, though, seems affected very little by the  $\beta$  grain size. The writer has found that it is possible to refine the  $\beta$  grain size only by cold working the slowly cooled alloy after it has transformed to  $\alpha$  plus  $\gamma$  and reheating to the  $\beta$ -phase field. Heating through the allotropic transformation, as in steel, seems to have no effect on the  $\beta$  grain size. Do the authors have any information on this point?

I cannot agree with the authors' statement in point 5 of the summary that "Even though the cooling of the specimen is interrupted by an isothermal holding at an intermediate temperature, the remaining beta can also be retained at room temperature by the subsequent quench." I have isothermally transformed a eutectoid specimen at 300°C for 1 hr and obtained no microscopic evidence of transformation. The specimen appeared to be all  $\beta$ , yet the X-ray diffraction pattern showed only  $\alpha$  and  $\gamma$  lines and no  $\beta$ . I also have obtained X-ray evidence that a quenched eutectoid  $\beta$  undergoes transformation on remaining at room temperature. I can cite many more very interesting and confusing X-ray results on this alloy, but my point is that the transformations of the  $\beta$  phase in the Be-Cu system are far from simple, and that what appears to be  $\beta$  may not always be  $\beta$ .

**J. T. Richards** (*Beryllium Corp., Reading, Pa.*)—The authors of this excellent work have identified three isothermal transformation products: Fine pearlite, coarse pearlite, and  $\beta$ . There is no indication, however, as to the structure in which the microhardness determination was made. It would have been of interest if microhardness curves had been plotted for each structure at the transformation temperatures producing more than one structure.

Although Raynor<sup>12</sup> has given the eutectoid temperature as 575°C based on four prior investigations, there is considerable evidence to substantiate the authors' claim that this value is too low. Masing and Dahl<sup>13</sup> found by microscopic investigation that a 6 pct Be-containing alloy was still homogeneous after quenching from 620°C, although there are indications of incipient decomposition. On the basis of microscopic and hardness tests by Ewing<sup>14</sup> the eutectoid temperature falls between 600° and 620°C. Borchers and Otto<sup>15</sup> claim that the eutectoid temperature may run as high as 50°C over the generally accepted figure (575°C), based on a dilatometric investigation with a maximum heating rate of 0.65°C per min.

Perhaps one of the most complete studies of the eutectoid transformation was conducted by Thomas.<sup>16</sup> From dilatometric investigations, an average of 620°C was obtained on heating at 0.5 to 1.0°C per min, while cooling at 1°C per min gave 601°C. Electrical resistance measurements on heating yielded 618°C. These results were checked by thermal analysis and values of 618°C (on heating at 4°C per min) and 601°C (on cooling at 5°C per min) were obtained. Thomas claims that the low values previously reported result from dilatometric curves being taken only for decreasing temperatures and at too rapid cooling rates.

In considering the above results together with those of the present authors (608°C), a range of 608° to 610°C is suggested for the eutectoid temperature instead of the accepted figure of 575°C.

There is good agreement on the hardness of the various structures between Ewing<sup>14</sup> and the present paper. For specimens quenched from 700° to 800°C,

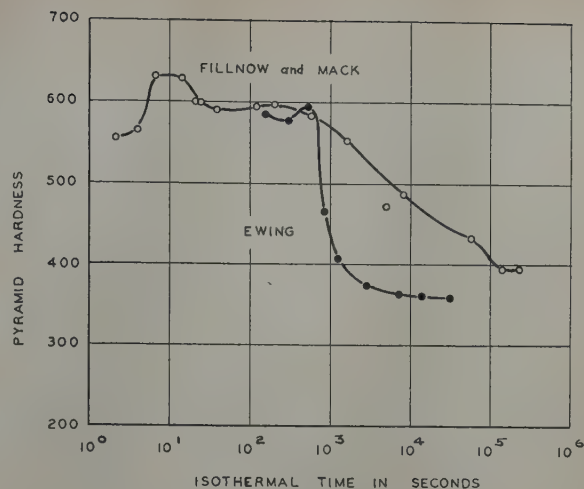


Fig. 38—Changes in hardness at 400°C.

Ewing obtained Vickers hardnesses ranging from 561 to 614 for the  $\beta$  phase, while the present authors give values from approximately 550 to 640. Ewing reports a hardness of 243 for a specimen heated at 570°C for 2½ hr, comparing with an approximate value of 245 in the present paper for the same time at an isothermal transformation at 550°C. As a matter of interest, Ewing found that the hardness of 243 obtained by heating for 2½ hr at 570°C increased to 566 upon further heating for 15 min at 620°C.

Although Ewing did not employ isothermal heating, his results obtained by quenching to room temperature followed by reheating give the same general trend. Fig. 38 superimposes one of Ewing's curves on the authors' Fig. 23.

**R. H. Fillnow and D. J. Mack** (authors' reply)—The writers wish to thank Messrs. Haynes, De Moss, and Richards for the additional information they have contributed. All results indicate that the currently accepted eutectoid temperature must be revised upwards to about 610°C.

The authors have repeatedly observed what Professor De Moss points out, i.e., that the  $\beta$  grain size in this alloy cannot be refined by simple heating through the transformation range, as is the case with steel. This phenomenon is well known in aluminum bronzes and is apparently the customary behavior in eutectoid transformations where neither component exhibits allotropy. Thus there are two types of eutectoid transformation as Harrington<sup>17</sup> has pointed out: The allotropic eutectoid and the plain eutectoid.

Unfortunately, the authors' X-ray diffraction studies were confined to the lamellar  $\alpha$  plus  $\gamma$  aggregates and hence we cannot comment on Professor De Moss' results regarding the transformation of  $\beta$  to  $\alpha$  and  $\gamma$  without change in microstructure. Such a transformation is certainly possible and may be associated with some of the transitory changes in microstructure that occur. We are in complete agreement with Professor De Moss concerning the complexity of the transformations in this system.

Professor Haynes has pointed out the objections to the simple mechanism proposed by the authors for the two pearlite reactions. The possibility of the fine pearlite being composed of metastable phases, say  $\alpha'$  and  $\gamma'$ , should not be ruled out until more definitive experiments have been performed. However, one need not rule out recrystallization of the  $\alpha$  because of strain energy requirements and the apparently logical assumption that at high temperatures this strain energy would be released by localized plastic flow for the following reasons:

1—"Recrystallization" of  $\alpha$  in an alloy containing 1.92 pct Be has been observed at 400°C.<sup>5</sup> Here the mechanism is a solution and redeposition of the precipitate at the advancing interface. The appearance



of the coarse pearlite suggests this mechanism of discontinuous precipitation.

2—Release of the strain energy might not be possible because of the rigidity of the lattice caused by its high solute metal content and the restraint imposed on the  $\alpha$  by the adjacent lamellae of  $\gamma$ . As a matter of fact, experiments now underway on the Cu-Sb eutectoid have shown that a quench of the high temperature body-centered tetragonal  $\beta$  phase into a salt bath held only 20° below the eutectoid temperature (436°) results in strain markings due to anisotropic contraction of the tetragonal phase. These strain markings later serve as sites for the precipitation of the stable end product phases.

It is believed that the apparently diverse views of Professor Haynes and the writers will coincide if the existence of metastable  $\alpha'$  and  $\gamma'$  or some transition lattice can be established, because there will then be an easy energy path for the reaction to follow.

No quantitative measurements have been made on the lamellae of either the coarse or fine pearlite. Both get finer as the transformation temperature is lowered, but no coarsening was observed below the nose of the transformation curves.

In answer to Professor Haynes' objection to the use of microhardness methods, the authors found that a very light load was necessary for obtaining hardness values of the retained  $\beta$ . With the heavier loads used, for example, with a Rockwell C scale, the indenter had a tendency to shatter the brittle  $\beta$ . For the sake of uniformity of data, microhardness determinations were used throughout.

The authors must remind Professor Haynes that microhardness determinations were not used to fol-

low the isothermal reactions. Any start or finish times, as given on the various hardness curves, were obtained solely through metallographic methods. Hardness data was obtained only for purposes of a qualitative correlation with metallographic data. Since this was the purpose of the hardness readings, several traverses were made across the specimen if two phases existed, and a mean value taken. In answer to Mr. Richards, this gave a very acceptable, reproducible hardness value. The variation in hardness values, shown on Fig. 30, was the largest spread found throughout the work. Approximately 90 pct of the hardness values obtained by the traverse method had a spread of only 10 or 20 points on the Vickers scale. The Rockwell scale was placed on the hardness plots in addition to the Vickers hardness scale only as a guide for those readers unfamiliar with the Vickers hardness numbers.

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## The Effect of Alloying Elements on the Plastic Properties of Aluminum Alloys

by J. E. Dorn, P. Pietrokowsky, and T. E. Tietz

DISCUSSION, R. M. Parke presiding

**A. I. Snow** (University of Chicago, Chicago)—In a footnote to their paper the authors cite the work of Ageev and Guseva on the distribution of the electronic density in aluminum and quote from *Chemical Abstracts* that: "Comparison between the experimental (structure factor) curves and the theoretical curves drawn for  $Al^{+}$  and  $Al^{+++}$  leads to the conclusion that in the metal crystal lattice, Al is present as approximately bivalent ions." The words in parentheses, "structure factor", which are evidently inserted by Dorn and coauthors, are misleading since what was compared were not structure factor curves but electron density curves, namely, the ones obtained by using the structure factors as coefficients in a three dimensional Fourier series compared with electron densities calculated for various assumed valence states. In a later paper Ageev and Ageeva use intensity data obtained by themselves, instead of from the literature as in the first paper, and this time arrive at a valence for metallic aluminum of approximately 2.5. The results of both papers by Ageev and coauthors concerning the valence of aluminum are open to serious question

since it has been shown theoretically<sup>25</sup> that no matter whether aluminum is mono-, di- or trivalent the atomic scattering factor curves in the range of observable X-ray diffraction maxima are identical. These atomic scattering factor curves only differ appreciably below the value of  $\sin \theta/\lambda$  of the first reflection that it is possible to observe (111). Therefore the structure factors and intensities of a given reflection will be identical for all three possible valence states and the use of the experimentally determined structure factors will lead to no knowledge of the valence states of aluminum no matter how mathematically manipulated. There are other serious objections to the treatment of the experimental data by Ageev and coauthors in these and other papers which I intend to discuss elsewhere.

**J. E. Dorn, P. Pietrokowsky, and T. E. Tietz** (authors' reply)—We wish to thank Dr. Snow for his interpretation of the results obtained by Ageev and Guseva on the electron density curves in metallic aluminum. They are looking forward with interest to Dr. Snow's paper on this subject.

<sup>25</sup> R. W. James: *The Optical Principles of the Diffraction of X-rays*. p. 303. (1948) London. G. Bell and Sons, Ltd. James points out the difficulty in obtaining the valence of aluminum by comparison of calculated and experimentally obtained atomic scattering factor curves but does not point out that this must also necessarily entail difficulty in obtaining valence values from electron density curves.

## The Properties of Some Magnesium-Lithium Alloys Containing Aluminum and Zinc

by Robert S. Busk, Donald L. Leman, and John J. Casey

DISCUSSION, R. M. Parke presiding

**P. D. Frost** (Battelle Memorial Institute, Columbus, Ohio)—I would like to comment on the statement on p. 946 of the paper, in which the authors say that increasing lithium increases stability. This is somewhat misleading. Refer, for example, to the 6 pct Al alloy in

Table III. Increasing the lithium from 3 to 12.5 pct results in a high strength alloy. This alloy attains its maximum yield strength in the quenched condition; subsequent aging at 180°F effects softening. When the lithium content is increased to 16 pct, an alloy is produced which has lower strength as quenched, but whose aging cycle at 180°F is somewhat slower than that of the Mg-12.5 pct Li-6 pct Al alloy. Thus, this alloy undoubtedly attains its maximum strength after aging a few hours at 180°F.

If aging were carried out for a much longer period



than 16 hr, it would be observed that the final strength, for a given aluminum content, would be higher as the lithium was decreased. This is demonstrated for an 8 pct Al alloy in Fig. 4. The alloy having 13.1 pct Li attains maximum hardness as quenched from 700°F. Increasing the lithium to 15.3 pct delays the aging cycle slightly, and the peak hardness occurs after about 1 hr at 200°F. The stability, however, is actually lowered.

When the lithium level is lowered to 8.8 pct, the hardness, as quenched, is lower. However, the aging curve is considerably flatter, and the hardness after 1000 hr at 200°F is higher than either of the higher lithium alloys.

**D. L. Leman** (authors' reply)—Mr. Frost's data on the extended aging of Mg-Li-Al alloys is an important contribution to this paper and is appreciated. However, it was not our contention that increasing lithium increases stability of properties over the entire range of lithium studied. This statement was made on the basis of alloys containing 12 and 16 pct Li, both of which have a wholly cubic structure. The exceptional high strength properties obtained in this alloy system are possible only with the predominately cubic alloys. The subsequent major loss of strength is associated with the high strengths produced. Alloys which have a predominately hexagonal crystal structure are definitely more stable than the cubic alloys but at a lower strength level as shown in Table III.

We also believe that the statement regarding the

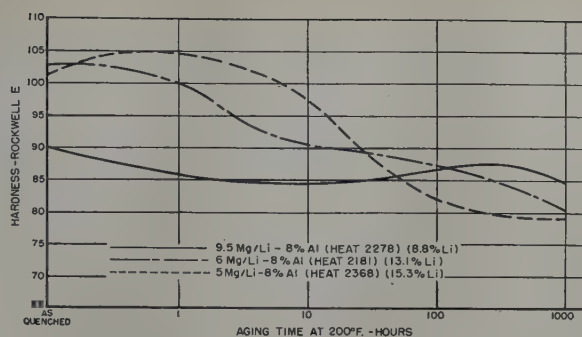


Fig. 4—Effect of lithium on aging Mg-Li-Al alloys.

effect of lithium content on property stability is applicable. High strength is produced by precipitation hardening and the question of stability is therefore dependent on the tendency of the alloy to overage rather than on its strength in the overaged condition. It is not uncommon for the strengths of age-hardenable alloys in other systems to equalize in the overaged condition even though the aging curves may differ considerably. The superiority of Mg-16 pct Li-10 pct Al over Mg-12.5 pct Li-10 pct Al (or Mg-15.3 pct Li-8 pct Al over Mg-13.1 pct Li-8 pct Al) in this respect is significant and would be expected to be even greater as the temperature of exposure is lowered.

## The Effect of Sodium Contamination on Magnesium-Lithium Base Alloys

by P. D. Frost, J. H. Jackson, A. C. Loonam, and C. H. Lorig

DISCUSSION, R. M. Parke presiding

**R. J. M. Payne and J. D. L. Eynon** (*J. Stone and Co. Ltd., Deptford, London, England*)—We at Deptford have worked on Mg-Li alloys since May 1947. It is hoped that a formal paper which will be largely concerned with the effects of impurities will be presented to the Institute of Metals (London) in the near future. Pending its publication we offer the following comments on this paper.

As the authors observe, the preparation of satisfactory Mg-Li alloys is largely a matter of securing freedom to a sufficient degree from the other alkali metals which are so often found in association with the basic metals. We too started with the LiCl-KCl flux and impure lithium, we changed to fluxes composed wholly of lithium salts, we refined our lithium by vacuum fusion until such time as the high grade lithium became available, we grew more watchful for impurities and became increasingly critical of our raw materials (including the magnesium) as the work proceeded. In our investigations we were greatly handicapped by the lack of reliable analyses, and it is only recently, and as a result of much careful work, that methods for determining the very small amounts of sodium and potassium, which we now know to be significant in alloys, have become available. Investigations carried out at the Admiralty Materials Laboratory, Holton Heath, Dorset, England, have put analytical procedures on a firm footing and we feel that we can now speak with confidence regarding the amounts of alkali metals which can be tolerated in the final alloys: We can also give tolerance limits for impurities in basic metals and salts. We agree that the principal difficulty in working with Mg-Li alloys is with sodium. As we see it, the main concern of the present authors has been to secure the full ductility of the material in the cast or wrought condition and to this end they have found it advantageous to reduce sodium contents to a low level. We have discovered a further reason for excluding sodium from melts of Mg-Li alloy and one which necessitates that the amount of this element be held at an even lower level. We have found that while alloys containing about 0.01 pct Na may in the cast condition show the full ductility

of which the material is capable, such alloys may be unstable and liable to develop intergranular weakness due to the precipitation of sodium. We have evidence that there is a very marked difference in the solubility of sodium in the  $\beta$  phase between temperatures of about 400°C and room temperature, and that alloys which were ductile as-chill-cast or as-wrought may embrittle very seriously on mild heating or even on standing at room temperature. To avoid these effects we consider it desirable to limit sodium to much smaller contents than those which just permit good elongation to be obtained in the cast or wrought state. The degree to which complex alloys are affected by sodium depends on the particular elements added to the basic Mg-Li alloy. From our own work we have seen that the sensitivity to sodium is considerably less marked in wrought than in cast alloys, and it may be for this reason that Frost and his colleagues have found as much as 0.03 pct Na unobjectionable in an alloy containing 9 pct Li and 4 pct Zn (Fig. 1): It is possible under certain conditions of heat treatment that this same alloy would have developed intergranular weakness through the precipitation of sodium. A difference in the sensitivity to sodium as between wrought and cast products would be understandable in view of differences in grain size: For an alloy of given sodium content, the concentration of sodium at the boundaries will obviously be less in the case of a fine grained material due to the greater area over which the impurity is spread. A tendency for sodium to seek grain boundaries has already been reported by Busk, Leman, and Casey.<sup>1</sup> These authors, however, refer specifically to ternary Mg-Li-Al and Mg-Li-Zn alloys and have not apparently realized that the same phenomena may be met in basic binary compositions. So far we have seen no report of solubility varying with temperature. We have made a conclusive demonstration of the solubility of sodium by heating to 400°C and quenching an alloy containing sufficient sodium as to cause it to break with zero elongation when tested as chill cast: The specimen thus heat treated was quite ductile.

We have spent much time, as have the American workers, in seeking methods of eliminating sodium



from melts, thus removing the need for very high purity in basic materials; success in this field has, however, been limited. We do not propose to pursue this topic at any length, but will record that we do not find the LiCl-LiF flux to have outstanding virtues as regards sodium removal; in fact we regard it as inferior to simple LiCl in this respect. We are aware that the chloride-fluoride flux has other advantages which make it preferable to the simple chloride in certain circumstances.

**H. M. Skelly** (*Aluminum Laboratories Ltd., Kingston, Ont., Canada*)—Have any tests been made for flux inclusions in melts of Mg-Li alloys prepared under a covering flux of 75 pct LiCl plus 25 pct LiF?

**P. D. Frost, J. H. Jackson, A. C. Loonam, and C. H. Lorig** (authors' reply)—It was a pleasure to receive the excellent discussion from Messrs. Payne and Eynon. The observation regarding the difference in solubility of sodium between 400° and 20°C is very interesting and may account for some of the hardness changes we have obtained in aging quenched binary alloys.

Most of our work has been with wrought alloys. It has been our experience that cast Mg-Li ingots must be hot worked considerably to develop good properties. The precipitation of sodium at the boundaries of coarse grains undoubtedly contributes to low ductility in castings. Of course, a wrought, fine grained structure usually has greater ductility than a cast structure, even in the absence of contaminating elements.

It is noteworthy that Messrs. Payne and Eynon found that LiCl removed sodium more effectively than the LiCl-LiF flux. We found that the LiCl-LiF flux was very effective. However, we believe that the efficiency of these various salt mixtures depends to a major extent on the sodium content of the salt as procured.

In reply to Dr. Skelly, fracture tests on cast ingots and wrought specimens rarely reveal flux inclusions in Mg-Li alloys. On the other hand, the alloys often become badly pitted under humid conditions. We are, at the present time, attempting to evaluate the effect of contaminating materials, such as flux, on corrosion resistance.

## Hydrogen Embrittlement of SAE 1020 Steel

by J. B. Seabrook, N. J. Grant, and Dennis Carney

*DISCUSSION, R. M. Parke presiding*

**G. A. Moore** (*University of Pennsylvania, Pittsburgh*)

—The authors are to be congratulated for making several very important additions to our information on the nature of hydrogen embrittlement. While it is pleasing that the relation of ductility to hydrogen content has been so closely checked with our previous work,<sup>10</sup> the agreement is perhaps more fortuitous than realized, since steels of quite different carbon content and structure are compared. The agreement emphasizes that the embrittling effect is mainly on the ferrite phase, while cases of disagreement, such as the occurrence of "permanent damage," re-emphasize the fact that hydrogen tends to be highly segregated, so that its effects must be more localized (microscopically) in the cast material than in these electrolytically charged cases. The hydrogen content to cause actual microcracks and thus decrease impact values, therefore, varies widely with structure and source of hydrogen.

A great advance has been made by the inclusion of the natural stress-strain data in the present paper. At the time of the earlier report, we did not realize the fallacy of using the metallurgically meaningless engineering values until too late to obtain the complete data, an omission which I have personally had numerous occasions to regret. Approximate determinations of the fracture stress did show a better correlation to hydrogen than the ductility measurements, but the lack of the stress-strain curves prevented a complete analysis of the effects occurring. The authors would be justified in discussing Fig. 5 in much greater length. The figure appears to justify analysis as follows:

The conclusion of Smith<sup>8</sup> that none of the hydrogen is in actual solution in the lattice is supported by the lack of hydrogen effect on the yield strength and hardness. The conclusion that after slight strain the hydrogen is occluded in rifts, mosaic disjunctions, or the tension sides of Taylor dislocations, and spreads these openings, is supported by the fact that the effect on the flow curve could be expressed as the addition, without dimensional change, of a plastic strain of 0.05 to 0.10, in line with earlier statements that "the effect of hydrogen is similar to that of a little cold working." This mode of occlusion is realized to induce tensile microstresses, largely triaxial, in the noninterrupted portions of the lattice structure, which stresses tend to interfere with flow. These stresses now may be

estimated for the first time from the information that the flow stress of charged bars lies about 6000 psi above that of uncharged bars. Presuming the actual value of the critical shear stress unaffected by hydrogen, then in the presence of a radial biaxial tension, either the maximum or octahedral shear stress laws require that the applied tensile stress be increased by the same amount to maintain flow. Thus the microstresses induced by the hydrogen here have a net unbalanced radial component averaging about 6000 psi, except at the immediate surface where they are noted to have been relieved by blistering. The unknown triaxial component in the axial direction, which balances out in testing, may be added to obtain the actual microstress, but since the observed flow stress does not increase with further addition of hydrogen after about 2 ppm (or 0.2 relative volume), it is unlikely that the stresses ever actually exceed 10 pct of the estimated 100,000 psi calculated on the assumption that the volume occupied by the precipitated hydrogen is negligible.

The old argument as to whether the embrittlement is due directly to the presence of the rifts, or to the microstresses around the rifts, therefore appears resolved. The fracture stress is lowered progressively by continuing increases of hydrogen content, with an observed loss of 40,000 psi at contents of 5 to 10 ppm. The idea that the actual strength of the metal remains constant and the 40,000 psi stress is supplied by the gas pressure is incompatible with the small and fixed effect on the flow stress, hence it is clear that only a minor portion of the embrittling action is due to the stress, while a major portion is due to the extension of the rift system, with its interruption of the coherency of the metal and obvious notch effects.

As this analysis is of necessity based on the published figure alone, perhaps the authors will be so kind as to check it against the unpublished data and investigate other interesting details. For example, it appears that hydrogen reduces the amount of uniform strain just enough that the stress at maximum load is not changed, which may help explain how the hardness can be unchanged while the tensile strength rises, and perhaps also why some observers find hydrogen to lower the tensile strength, some to raise it, and many to find it to have no effect. Certainly the publication of more natural stress-strain data in connection with hydrogen embrittlement problems will be a very important addition to our understanding of the mechanism involved.



**J. B. Seabrook, N. J. Grant, and D. Carney** (authors' reply)—The authors thank Dr. Moore for his discussion and interesting analysis. It may turn out that the agreement as to minimum hydrogen required for maximum embrittlement is fortuitous. If the embrittling effect is truly mainly in the ferrite phase, however, it is conceivable that further experiments with the embrittlement of ferritic material will show agreement with the figure of 5 ppm at maximum embrittlement for the hot-rolled condition.

Because hydrogen segregates at the grain boundaries and interdendritic zones, it is expected that hydrogen will be much more segregated in cast materials, resulting in permanent damage. Accordingly, low values of hydrogen in a cast material need not signify freedom from damage, especially if the hydrogen has had an opportunity to diffuse out.

We hesitate to make specific far-reaching conclusions regarding all the information to be derived from the true tensile strength curves. We are not sure that one can express the differences in the flow curves as differences in strain; the effect may rather be looked upon as an increase in flow stress due to the occlusion of hydrogen shortly before the increase is measured. In this respect the effect of hydrogen would definitely not be "similar to a little cold work."

We agree that the difference in fracture stress of 40,000 psi is not supplied by gas pressure. High pressures can, however, be exerted. The surface bursts which occur when more than about 6 ppm of hydrogen is charged indicate the tensile strength of the cold-worked (from machining) steel surface is exceeded.

As much a reappraisal of all the data as time would permit has not disclosed sufficient evidence to extend our analysis except for one factor. It should be emphasized that the division of high and low curve samples was on a general basis, and no definite curve of increased flow stress vs. hydrogen content was obtained with the accuracy of our experiments. Likewise, the proposition that stress at maximum load is not changed cannot be supported by our data. However, for the slow strain rate specimens, the strain at maximum load was noticeably less than for the usual rate tests. Perhaps some hardness reading change would be noted in hydrogen-charged specimens if the hardness tests were performed at a slow rate of application of load.

**P. Bastien and P. Azou** (*Ecole Centrale des Arts-et-Manufactures; Laboratoire de Physique des Métaux, Paris, France*)—We think that the measurement of the volume of hydrogen extracted under mercury from steel specimens (previously treated with this gas by pickling or electrolytic action) by degassing at room temperature does not lead to systematic errors when the usual precautions required for mercury handling are taken. Some air can be entrained by specimens when put in mercury, but tests made by one of us indicate that the collected gas contains at least 99 pct hydrogen. Hydrogen concentration in pickled or electrolytically treated specimens is more heterogeneous than in specimens as received from the steel mill. In the first case, it is particularly high at or close to the metal surface. Therefore, we think that degassing by heating in vacuo may be inadequate, for a great part of the hydrogen may be expected to be lost due to the reduced pressure prior to the actual measurements. We should appreciate hearing some details of the degassing practice used by the authors.

Hydrogen collected under mercury at room temperature is the easily diffusing gas which causes embrittlement of pickled or electrolytically treated specimens. One of us has given evidence that a relation exists between the volume of the easily diffusing hydrogen and the brittleness of the metal.<sup>24</sup>

We are particularly interested in the results obtained by the authors with true stress-true strain tensile tests. We also have plotted true tensile curves for an annealed 0.15 pct C steel both with and without hydrogen. The main results have been presented<sup>15</sup> at

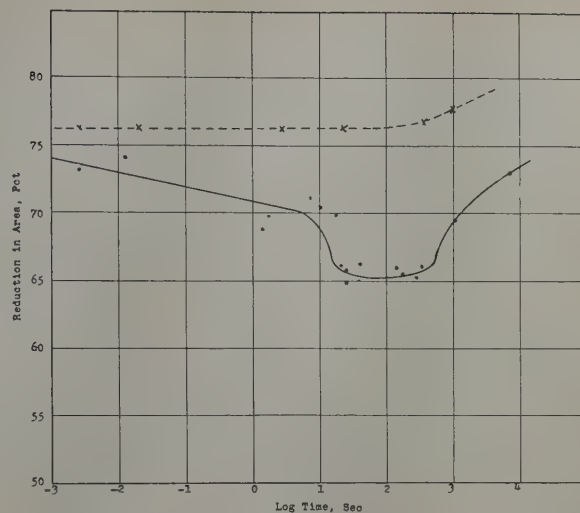


Fig. 9—Effect of strain velocity on reduction of area.

Lower curve shows the effect of hydrogen treatment on the reduction of area of the untreated steel in the upper curve at various rates of straining.

the French Academy of Sciences on April 4 and May 9, 1949. The conclusions reached by the authors are in good agreement with ours. Hydrogen influences only the true rupture stress. The true tensile curves are superimposable whether the steel contains hydrogen or not, but the fracture will occur at a lower true stress when there is hydrogen in the steel; a fact in agreement with a smaller reduction in area. Moreover we have shown that when the testing temperature decreases, the true breaking stress is lowered for a pickled steel. This fracture is semibrittle for ordinary and brittle for hydrogen-bearing steels; the phrases "semibrittle" and "brittle" being used in accordance with Shevandin's work.

In addition we have shown that: 1—Iron and steel brittleness due to hydrogen disappears below  $-110^{\circ}\text{C}$  and reappears reversibly by heating above this temperature.<sup>16</sup> 2—The influence of the gas on the elastic modulus and damping capacity will be smaller if the test used to determine the property being studied causes smaller elastic deformation and apparently is reduced with increasing elastic strain during the test.<sup>17</sup> 3—In tensile tests at room temperature with the duration of the test ranging from 1/150 sec to 2 hr 20 min, hydrogen has no effect on the capacity for deformation at high speeds, its effect becoming a maximum for times between 10 sec and 30 min, then becoming gradually smaller with low rates of straining<sup>18</sup> as shown in Fig. 9.

Our views agree with the authors that hydrogen in the proton condition in the iron lattice<sup>19</sup> has, within the elastic range, no effect on the properties of the metal. Under plastic deformation, the hydrogen, probably diffusing through the motion of dislocations, will collect at the volumetric defects at various locations in the metal where, when it can recombine as molecular hydrogen, it will develop triaxial forces which resist deformation by slip and cause hydrogen embrittlement. Since segregation requires diffusion, it will not occur at the lowest temperatures; below  $-110^{\circ}\text{C}$  for our tests, where thermal agitation is too small, nor with high rates of plastic straining when the time is too short for mass displacement of protonic hydrogen.

This is the reason why hydrogen does not alter significantly the impact resistance of steels, which we have measured over a temperature range from  $-70^{\circ}$  to  $18^{\circ}\text{C}$  using standard type specimens. Similarly it is not surprising that there is no difference in the hardness of test pieces of the same steel with and without hydrogen. In hardness testing, the rate of straining is very high and the plastic deformation is

completed before the time required for hydrogen segregation and resultant action.

**J. B. Seabrook, N. J. Grant, and D. Carney**—We are particularly pleased to find our results in such good agreement with the results of Messrs. Bastien and Azou. Our experience with degassing under mercury has not been too satisfactory. Frequently we found large disagreement between values so obtained and those obtained by vacuum fusion in an iron-tin bath. Regarding the degassing techniques used in this work, Messrs. Bastien and Azou are referred to the two papers by Carney, Chipman and Grant, refs. 11 and 12 of the paper. In this connection we believe that the method described in the above papers is by far the most accurate, reliable, rapid, and simple method presently available for hydrogen analysis.

It is difficult to conceive that the so-called "easily diffusing hydrogen" is anything other than the hy-

drogen which occupies the outer position of the specimen.

The absence of a hardness effect in view of the rapid rate of straining during the test would certainly be a feasible explanation as suggested by Messrs. Bastien and Azou.

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## Aging Characteristics of Magnesium-Lithium Base Alloys

by P. D. Frost, J. G. Kura, and L. W. Eastwood

DISCUSSION, R. M. Parke presiding

**D. L. Leman** (Dow Chemical Co., Midland, Mich.)—The presentation of this paper is indicative of the continued interest in the high strength properties of some of the ultra-light Mg-Li base alloys. The general observations on the problems of property instability and lack of ductility in the high strength alloys is in close agreement with the results of work done at The Dow Chemical Co.<sup>4</sup>

The authors mention that the alloy 9.5 Mg/Li-7 pct Al-3 pct Sn may have resistance to stress-corrosion cracking nearly equal to that of AZ31A-H24.\* Using a different testing method, we find it to be appreciably less resistant. The stress-time curves for bars spring-loaded in simple tension and exposed up to four years in a rural atmosphere are given in Fig. 13. Although the time before failure occurring at a given stress-level varies considerably for AZ31A-H24, the failures for 9.5 Mg/Li-7 pct Al-3 pct Sn all took place within such a short time that no significant variation would be expected on more extensive testing. The difference between the two alloys would not be readily apparent at stresses as high as those reported in the paper, because failures occur in both alloys in a comparatively short time. For details of the testing method used and other factors affecting stress-corrosion testing see Loose and Barbican.<sup>5</sup>

We have also tested the creep characteristics of 9.5 Mg/Li-7 pct Al-3 pct Sn at 95°F. The sustained-stress which will produce 0.1 pct extension in 100 hr is 15,000 psi as compared to 18,000 psi for AZ31A-H24.

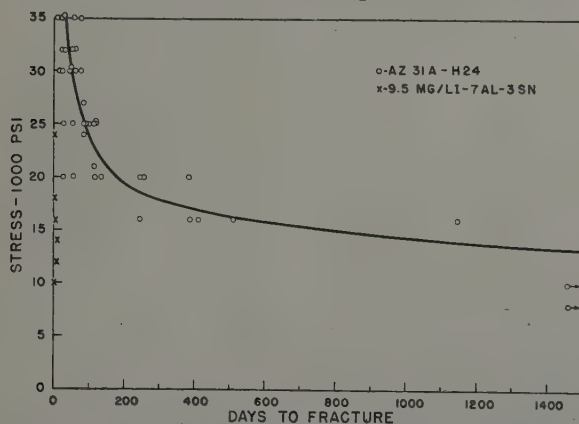


Fig. 13—Stress corrosion of AZ31A-H24 and 9.5 Mg/Li-7 pct Al-3 pct Sn.

It may be well to mention our conclusions at The Dow Chemical Co. based on the extensive investigation of Mg-Li base alloys. Without going into detail on specific compositions it can be said that there are three distinct classes of alloys as follows:

1—Soft ductile alloys which have a cubic or predominately cubic crystal structure. These are outstanding with respect to formability and toughness at a tensile and compressive yield strength level of 20,000 to 25,000 psi.

2—High strength alloys which have a cubic or predominately cubic crystal structure. These compositions may also be of the Class 1 type in the soft condition but their strength can be trippled by precipitation of the MgLi<sub>2</sub>X phase.

3—Intermediate strength alloys which have an hexagonal or predominately hexagonal crystal structure. Maximum strength in these is developed by cold working or the combination of heat treating, cold working, and aging. The typical tensile and compressive yield strength level is 40,000 to 45,000 psi.

Many of the compositions studied possess interesting properties in one respect or another, but none as yet have been found to have a suitable combination of mechanical properties, secondary properties, and service characteristics which would warrant acceptance as a commercial product. In particular the soft ductile alloys have poor creep resistance, the high strength alloys soften on continued exposure at slightly elevated temperatures and in general are quite brittle in the strong condition, and the intermediate strength alloys are characterized by low notch toughness and high stress-corrosion sensitivity.

The approach to the development of a usable alloy of maximum strength must be through a fundamental study of the mechanism of MgLi<sub>2</sub>X hardening. Creep, toughness, stress corrosion, and possibly other secondary properties should be studied on the basis of alloy design.

**P. D. Frost, J. G. Kura, and L. W. Eastwood** (authors' reply)—Mr. Leman's contribution to this paper is greatly appreciated. It is assumed that the stress corrosion and creep tests to which he refers were con-

\* AZ31A-H24 is the newly accepted ASTM designation for AZ31X-h.

<sup>4</sup> R. S. Busk, D. L. Leman, and J. J. Casey: The Properties of Some Magnesium-Lithium Base Alloys Containing Aluminum and Zinc. *Trans. AIME* (1950) **188**, p. 945; *Journal of Metals* (July 1950).

<sup>5</sup> W. S. Loose and H. A. Barbican: Stress Corrosion Testing of Magnesium Alloys. Symposium on Stress Corrosion Cracking, ASTM-AIME (1945).



ducted on sheet specimens of the 9.5 Mg/Li-7 pct Al-3 pct Sn alloy prepared at Battelle and sent to Dow for this purpose.

It is difficult to correlate stress-corrosion data obtained by two different methods of testing, particularly where so few specimens are involved. The objections to the bending method of loading are recognized. However, these do not offset the usefulness of this type of test, particularly for materials, such as the 9.5 Mg/Li-7 pct Al-3 pct Sn alloy, whose compressive and tensile yield strengths are equal.

Although the Dow and Battelle results are in fair agreement for the highly stressed specimens, the discrepancy between the results for the lower stressed specimens must await further tests for clarification.

We do not have creep data for the 9.5 Mg/Li-7 pct Al-3 pct Sn alloy. However, we are evaluating the creep and stress-rupture characteristics of 9.5 Mg/Li-7 pct Al-1 pct Sn alloy sheet. Under a stress of 30,000 psi, one specimen failed after 58½ hr. Under a stress of 20,000 psi, one specimen has elongated a total of 0.4 pct in 100 hr, including the initial deformation. It is assumed that the Dow values represent total elongation in 100 hr, and not creep rate.

The following additional remarks concerning the corrosion resistance of Mg-Li base alloys may be of interest. Panels of several alloys have been exposed to the semitropical marine atmosphere at Daytona Beach, Fla., since June 7, 1950. The corrosion rates obtained to date for these alloys are given in Table VIII.

One of the authors carries a pocket piece of an alloy containing 87 pct Mg-9 pct Li-4 pct Zn. This specimen

Table VIII. Corrosion Rates of Some Mg-Li Alloys

| Alloy                                  | Weight Loss Rate After Exposure Time Indicated |                  |                                         |                  |                                         |                  |
|----------------------------------------|------------------------------------------------|------------------|-----------------------------------------|------------------|-----------------------------------------|------------------|
|                                        | 2 Months                                       |                  | 4 Months                                |                  | 8 Months                                |                  |
|                                        | Mg per<br>Dm <sup>2</sup><br>per<br>Day        | In.<br>per<br>Yr | Mg per<br>Dm <sup>2</sup><br>per<br>Day | In.<br>per<br>Yr | Mg per<br>Dm <sup>2</sup><br>per<br>Day | In.<br>per<br>Yr |
| 9.5Mg/Li-7 pct Al-1 pct Sn             | 4.4                                            | 0.0036           | 6.25                                    | 0.0051           | 5.15                                    | 0.0042           |
| 9.5Mg/Li-7 pct Al-1 pct Mn-0.05 pct Sn | 2.35                                           | 0.0020           | 3.8                                     | 0.0032           | 3.6                                     | 0.0030           |
| 9Mg/Li-5 pct Al-8 pct Zn               | 1.75                                           | 0.0014           | 1.5                                     | 0.0012           | 1.15                                    | 0.0010           |
| AZ31A-H24                              | 1                                              | 0.00081          | 1.05                                    | 0.00084          | 0.9                                     | 0.00077          |

lay on the author's desk in New York City for four years, and for one year has been in contact with pocket keys and other metallic objects. Most of the surface has acquired a thin, dark, protective layer, while the edges remain bright.

The classification suggested by Mr. Leman for the three types of Mg-Li alloys is a convenient one. Although none of the alloys are yet ready for commercial applications, some may be suitable for special applications where low weight is an important factor. For structural purposes, we believe that the "intermediate strength" alloys of Class 3 offer the greatest promise.

## Hydrogen Solubility in Aluminum and Some Aluminum Alloys

by W. R. Opie and N. J. Grant

DISCUSSION, M. Bever presiding

**W. Baukloh** (Bengal Engineering College, Howrah, West Bengal, India)—On p. 1239 of their paper, the authors mention that their results are contrary to evidence presented previously by Baukloh and Oesterlen who observed a minimum in the curves for the solubility of hydrogen in Al-Cu, Al-Si alloys. Attention

may be drawn to the publication by Baukloh and Redjali<sup>9</sup> on hydrogen solubility in aluminum with some alloying elements (Co, Cu, Cr, Fe, Th, Ti, and Sn). The effect of copper published by Baukloh and Redjali were found to be similar to the results obtained by the authors.

**W. R. Opie and N. J. Grant** (authors' reply)—We wish to thank Professor Baukloh for the above information which was not available at the time of publication.

<sup>9</sup> W. Baukloh and M. Redjali: *Metallwirtschaft* (1942) 21, pp. 633-688.

## Dendritic Crystallization of Alloys

by B. H. Alexander and F. N. Rhines

DISCUSSION, M. Bever presiding

**R. W. Ruddle and A. Cibula** (British Non-Ferrous Metals Research Association, London, England)—We have been pleased to see this study of a sadly neglected subject and would like to compliment the authors on an interesting piece of work. In interpreting the results of their investigation the authors suggest that the dendrite arm spacing is governed primarily by heat transfer factors, specifically the ratio "heat of fusion/thermal diffusivity." We think however that, although they have discussed them very fully, the authors have not attached sufficient importance to the effects of concentration gradients in stifling the growth of budding dendrite arms and thus controlling the spacing of those which are able to grow. They state that no direct correlation exists between the arm spacing and freezing range and other constitutional factors, but surely no direct correlation is to be expected since the concentration gradients set up round a growing crystallite and their growth restricting effect should be controlled not only by the freezing range, but also by the slopes of the liquidus and solidus curves and by the rates of diffusion of the solute element in the melt. Unfortunately it is not possible to evaluate the effects of these factors from the information available.

The authors say that: "Because the diffusion of heat and the diffusion of matter obey similar rate laws, it

follows that these factors should support each other in their influence on the crystallization of alloys." If the authors mean by this merely that both these effects can restrict the growth of crystals, we are in agreement; but we would point out that both these effects cannot control the rate of growth at the same time. If the growth of an isolated dendrite in an undercooled melt is controlled by heat diffusion, then at first heat must be liberated during solidification faster than it can diffuse into the surrounding liquid; this will result in the setting up of a heat barrier round the growing crystallite, which will then limit the rate of crystal growth. Conversely, if the growth of the dendrite is controlled by the diffusion of metal atoms, a concentration barrier will be produced which will again limit crystal growth; in this case the liberation of heat of fusion must lag behind the extraction of heat by the surrounding melt. Clearly, both factors cannot control the growth of the individual dendrite at the same time.

Our own tentative picture of the mechanism of solidification in pure metals and alloys is as follows. The rate of growth of an isolated crystallite in an undercooled pure metal melt must be limited by the rate of heat diffusion into the liquid, for, as the authors state, concentration gradients are impossible in pure metals. However, the crystals growing in a molten pure metal rarely are isolated in the melt but are normally



attached to the mould wall from which they grow in a columnar manner towards the center of the casting. It follows that the heat liberated during solidification escapes through the solid wall of columnar crystals instead of into the liquid metal (which, except at the onset of solidification, is at or above the freezing point). The rate at which heat flows through the solid wall and consequently the rate of growth of the wall is governed by the rate at which the mould extracts heat.

This mechanism, we think, also must apply to dilute alloys which solidify in a columnar manner and in which the concentration gradients are too small to be effective. As the proportion of solute increases, however, a critical concentration is reached beyond which the growth-restricting effect of the concentration gradient exceeds the limitation on growth imposed by the rate of heat abstraction by the mould. Beyond this critical concentration, therefore, the mould removes more heat than is being liberated by solidification on the existing crystals; when this happens the melt in front of the initial dendrites undercools and crystallization begins at fresh nuclei in the interior of the melt, as has been observed with aluminum alloys.<sup>15</sup> This change in the mechanism controlling the rate of crystal growth is accompanied by a changeover from a columnar to an equiaxial structure. The concentration at which the change takes place is dependent upon the rate of heat abstraction by the mould, a high rate causing the changeover to take place at lower concentrations.

Because of the absence of a heat or concentration barrier in a metal of high purity solidifying in a columnar fashion as described above, the tendency towards dendritic growth is small and depends upon the fact that deposition of metal atoms from the liquid takes place preferentially on certain facets of the growing crystal. The absence of marked dendritic growth in solidifying pure metals is illustrated by the fact that when metals of high purity (e.g., 99.99 pct pure Al) are slush-cast in sand moulds the solid shell remaining in the mould has a smooth surface, whereas a metal of lower purity (e.g., commercially pure aluminum) leaves a shell whose surface is roughened by the tips of protruding dendrites. The development of concentration gradients in the presence of a solute element greatly enhances the tendency to dendritic growth, and the spacing of the dendrite arms presumably increases with increase in the gradients, much as described by the authors on p. 1271. However, as stated above, we do not agree with the authors when they suggest (p. 1272) that the controlling gradients are heat gradients and not concentration gradients. We doubt whether an apparent rough correlation of the kind shown in Table VIII, between the dendrite arm spacings and the ratio "heat of fusion/temperature diffusivity" establishes conclusively that heat gradients control the dendrite spacing, for it is likely that both heat and concentration gradients follow the same general trends with increasing concentration of solute element. In any case, analysis of the figures for the Cu-Ni and Cu-Sn series of alloys shows that the apparent correlations are not statistically significant, the probabilities that the apparent correlations arose by chance both exceeding 0.05; (we are adhering to normal statistical practice in regarding correlations as nonsignificant when the chance probability is greater than 0.05). It should however be stated that when all the figures for the Cu and Ni-base alloys are considered together, a correlation which is on the borderline of significance is found, the chance probability lying between 0.02 and 0.01.

Finally, we wonder whether the authors in their reply could give some further details of the way in which they measured the dendrite spacings of the different alloys. In particular, the description and micrographs in the paper do not make it clear what they regarded as "fully developed arms" and what as "stunted side arms." We should like to draw the authors' attention to a recent paper by Kostron<sup>16</sup> who measured the "cell size" of a large number of aluminum alloys. So

far as we can see the cell size measured by Kostron is essentially the dendrite spacing measured by the authors. If this is so, the two sets of measurements are completely at variance for in all cases the cell size measured by Kostron decreases with increase in the amount of alloying element.

**A. Hultgren** (*K. Tekniska Hogskolan, Valhallaragen, Stockholm, Sweden*)—This paper is a welcome contribution in a field where altogether too little is known and understood with certainty.

In their attempt at assessing a value for the average dendritic spacing at a given distance from the surface of an ingot, the authors often encountered a mixture of types of dendritic branches with different spacings, as pointed out on p. 1268. It is suggested that this may be due to two or more families of dendritic branches forming in succession at the same place.

In an investigation of solidification structures in 1.10 pct C steel ingots of commercial size<sup>17, 18</sup> it was found that the growing skeleton of each columnar crystal was built up of a number of parallel cruciform stems—plates intersecting at right angles—from which, at a later stage, secondary and tertiary rod-shaped branches developed, also in tetragonal directions. The spacing of the stems as seen in the cross-section of a crystal was considerably coarser than that of the rods. Whereas the former spacing appeared to increase by steps from root to tip of a columnar crystal, the latter increased continuously from surface to axis of the ingot, with no distinction between columnar and free crystals. The continuous lines seen here and there in the authors' Fig. 1 may be sections of plate-like branchings of columnar crystals whereas short, more closely spaced lines may be sections of secondary branches. In such case, sections parallel to the surface may be instructive. It is not, of course, suggested that the features described are necessarily present in all alloys with dendritic structure.

In Tables II, III, and V columnar and equiaxed grain sizes are both given. Does this mean that both types of grains were generally present at position (*m*)?

The authors' detailed picture of the mechanism by which dendritic branching develops appears plausible and, apart from the concept of successively formed idiomorphs, agrees well with an earlier attempt.<sup>19</sup>

Accordingly, and a little differently expressed, it may be said that the dendritic spacing at any point of an alloy crystal is determined mainly by the following two factors: 1—The linear rate of growth of the corner or main stem of the crystal as largely influenced by the degree of undercooling, and 2—the rate of diffusion of the alloying element. In a pure metal heat conductivity would take the place of the second.

As freezing continues inwards and the rate of growth is gradually retarded the shielding effect exerted by the enriched mother liquor gains upon the growing stem and the dendritic spacing is coarsened.

In the many cases where an alloying element was found to coarsen the spacing two factors may act in this direction: 1—Decreased rate of growth owing to lower bulk heat conductivity, and 2—increased diffusion distance and extended shielding effect owing to steeper concentration gradient in the mother liquor; the lower heat conductivity might be expected to have a local effect tending to decrease the spacing but this is probably overshadowed by 1 and 2.

The difference in spacing between primary and secondary branchings at the same place probably results from the cooling rate at any point increasing all the time as the freezing range is passed, the change in composition of the mother liquor meanwhile being of less importance.

The authors' statement that it is only when crystallization proceeds rapidly that dendritic growth is encountered seems to require some qualification.

In steel ingots of large sizes, coarse dendritic free crystals are found in the central region. Their branches have rounded contours, probably resulting from diffusion of alloying elements and surface tension. When



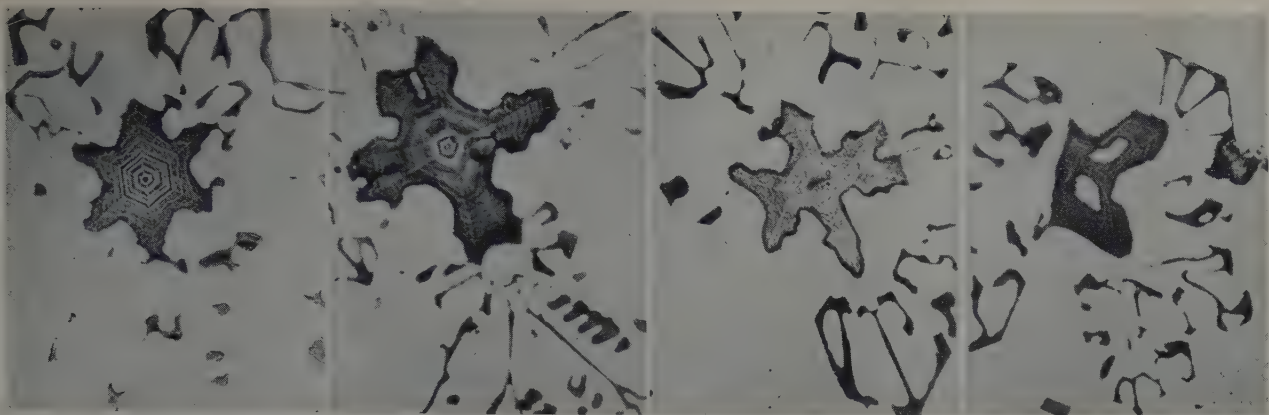


Fig. 11 (left)—Large constituent primary Al-Cu-Fe-Mn phase; smaller dark constituent forms binary eutectic with Al solid solution. The change from the hexagonal mode of growth occurs with depletion of chemical concentration in liquid phase. X500.

Figs. 12 (left center), 13 (right center), and 14 (right)—Influence of the "principal" planes of primary crystallization upon the mode of crystallization of the eutectic phases. Area reduced approximately 80 pct for reproduction.

the dendritic spacing reaches the same order of magnitude as the size of the crystal, so-called globular structure results. There is a smooth transition between dendritic and globular structure. The latter may be produced in ordinary steel ingots by suitable stirring<sup>15</sup> or, probably, by other methods of inoculation. I should be very much surprised if an idiomorphic  $\delta$  or  $\gamma$  Fe crystal were produced by crystallization in molten steel.

**H. Czyzewski** (University of Illinois, Urbana)—The writers have given an excellent report of their study in this field, and this discussion is made only as a small contribution to the writers' extensive work. The statement is made in the paper to the effect that the intrusion of a second solid phase, such as appears in richer alloys of eutectic and peritectic types, seems to be without influence upon the dendrite dimensions. This is presumed to be because the establishment of the dendrite pattern precedes the crystallization of the low melting phases.

It is suggested in this discussion that the writers' conclusion holds true for the early stages of crystallization but that in the final stages there would be an influence on dendrite dimensions due to the large chemical-concentration gradient from the solid dendrite to the core of the remaining liquid phase. Because the writers reported mostly on alloys in which the primary crystals were dominant, the effect in the final stages of primary crystallization of the second phase, that is the liquid, on the primary phase was not observed. The schematic representation (Fig. 10 of the paper) shows that there is an effect on mode of crystal growth, and therefore on dendrite dimensions, which is a function of velocity of the growth. The velocity of growth is a function of, among other things, the chemical concentration in the liquid adjoining the growing crystal. The writers conclude that the rate of heat transfer is probably of greater importance than is the rate of material transfer in establishing the dendrite spacing in metal systems. This conclusion is justified by the data only in the cases in which the liquid phase can continue to produce the primary solid phase.

A study of multiphase alloys requires modifications of these conclusions of the writers. For example, Fig. 11 shows a primary crystal identified as the Al-Cu-Fe-Mn phase which occurs in certain cast aluminum alloys of a commercial grade.\* The primary crystal shows a series of concentric hexagons of quite regular shape with straight sides and sharp corners. The writers made the statement that "corner rounding" must be expected. This rather common idea is not justified on the basis of Fig. 11. Also, the departure from the hexagonal mode of crystallization in this case does not occur as a function of heat transfer but rather as a function of material transfer and the depletion of the liquid phase. It

appears, therefore, that the second phase can exert an influence on the dendrite dimensions.

Conversely, it also may be concluded that the mode of solidification of the primary phase can exert an influence on the mode of solidification of a secondary phase, and therefore on the dimensions of the secondary phase. For example, in Fig. 11 not only the faces of the hexagons are defined but also apparent are the planes passing from the edges of the hexagons through the longitudinal axis of the hexagonal prism. The formation of these "principal" planes of crystallization is subject to interesting speculation. However, these principal planes have an influence on secondary crystallization, in the eutectic in this case, as seen in Figs. 12, 13, and 14.

Perhaps, the following conclusions may be considered. If the rate of material transfer is not greatly affected during the process of primary crystallization, then the rate of heat transfer regulates the dendrite dimensions. However, if the rate of material transfer varies greatly during the process of primary crystallization, then the primary dendrite dimensions and secondary phase dimensions will be affected.

**B. H. Alexander and F. N. Rhines** (authors' reply)—We thank the discussors for their interesting and valuable contributions to this paper. One main point that is brought up repeatedly in the discussion is whether heat flow or material flow is of greater influence on the dendritic growth in alloys. For the reasons given in the paper, we believe that heat flow is the more important, although we recognize that more work must be done before we can be sure.

It should be emphasized that the spacings we measured were what we considered to be the primary arm spacings which are established early in the course of freezing. The formation of secondary and tertiary dendrite arms and their change in shape due to spheroidization was not studied. It is the smaller size of these later generations of arms that determine the "cell-size" measured by Kostron. It is interesting that cell size varies with concentration in a different manner than the arm spacing; we can think of no good explanation for this, although the concentration and temperature would not be expected to be the same during the formation of the later arms as it was when the primary arms formed. We would estimate that the arm spacing in a given alloy is from 2 to 20 times the "cell size."

The grain sizes listed in Tables II, III, and V are the average width of columnar grains or the diameter of equiaxed grains; both types of grain were not found at the same position in an ingot.

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- <sup>17</sup> *Journal Iron and Steel Inst.* (1929-II) **120**, p. 69.
- <sup>18</sup> *Jernk. Annaler* (1930).
- <sup>19</sup> Pp. 77-79 of ref. 15.

\* The constituent was identified using the procedure in Mondolfo's *Metallography of Aluminum Alloys*. Only one etchant, 20 pct  $H_2SO_4$ , revealed the internal structure of this phase as shown in the accompanying micrographs. The etching action produced a relief effect which was deliberately accentuated in photographing and printing.

# The Crystal Structure of V<sub>3</sub>Co

by Pol Duwez

IN the course of an investigation of the V-Co system, two intermediate phases were found. One of these phases corresponds approximately to the stoichiometric composition VCo and is isomorphous with the sigma phase in the Fe-Cr system.<sup>1</sup> The second phase has the composition V<sub>3</sub>Co; its crystal structure is described in the present note.

The alloys were prepared by mixing the two metals in the powder form, pressing a small disk weighing about 5 g at 80,000 psi, and arc melting this disk on a water-cooled copper plate in an atmosphere of pure helium. The details of this technique have been described.<sup>2</sup> The vanadium powder was obtained from Westinghouse Electric Corp., Bloomfield, N. J. This powder is probably of very high purity, since when it is properly sintered or melted in the above-mentioned arc furnace, ductile specimens are obtained. The cobalt powder, from Charles Hardy, Inc., New York, contained 0.5 pct Ni, 0.1 pct Cr, and traces of Si and Fe.

After melting, the V<sub>3</sub>Co samples were sealed in evacuated quartz tubes and homogenized for ten days at 800°C. Powder diffraction patterns were obtained with a 14.32 cm diam camera, using K $\alpha$  copper radiation. The patterns were readily indexed on the basis of a primitive cubic lattice with a parameter equal to 4.675Å. The density, determined by the immersion method, was 6.71 g per cu cm; hence the number of molecules per unit cell is approximately 1.95; i.e., 2.

At this point, the possibility that the structure might be that of beta tungsten<sup>3</sup> became apparent. The beta tungsten structure is described as follows:

Space group O<sub>h</sub> — *Pm*3*n*

2 Co in (a) : 000;  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{2}$

6 V in (c) :  $\frac{1}{4}$ 0 $\frac{1}{2}$ ;  $\frac{1}{2}$   $\frac{1}{4}$ 0; 0 $\frac{1}{2}$   $\frac{1}{4}$ ;  $\frac{3}{4}$ 0 $\frac{1}{2}$ ;  
 $\frac{1}{2}$   $\frac{3}{4}$ 0; 0 $\frac{1}{2}$   $\frac{3}{4}$

(*hhl*) reflection present only if *l* = 2*n*.

Assuming this structure to be the correct one, intensities were computed by means of the usual equation:

$$I \propto p |F|^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

where *F* is the structure factor,  $\theta$  the Bragg angle, and *p* the multiplicity factor. The observed and calculated values of  $\sin \theta$  and the intensities are given in Table I. The agreement between the observed and the calculated  $\sin \theta$  is good and there are no flagrant discrepancies between the calculated intensities and those estimated visually. The (*hhl*) reflections for which *l* is odd are not observed, as required by the space group. In addition, the (410), (430), and (531) reflections are missing as expected, because of the special (a) and (c) positions in O<sub>h</sub>. However, six reflections—(110), (220), (310),

(411), (422), and (510)—which have very weak computed intensities were not observed. For these reflections, the structure factor is proportional to the difference between the scattering factors of the two atoms in the structure. Since the scattering factors of vanadium and cobalt are not very different, these reflections are weak. However, by using K $\alpha$  chromium radiation, whose wavelength is just above the absorption edge of vanadium, the effective scattering factor of vanadium may be decreased by one or two units; consequently the difference between the cobalt and vanadium scattering factors is increased. It was, indeed, found that in a powder pattern taken with chromium K $\alpha$  radiation, the three reflections (110), (220), and (310) were actually present. The three other reflections (411), (422), and (510), with spacings smaller than half the wavelength of chromium K $\alpha$ , were obviously not obtainable with chromium radiation.

All the experimental results appear to confirm the beta tungsten structure for V<sub>3</sub>Co. In this structure,

Table I. Diffraction Data for V<sub>3</sub>Co

| <i>hkl</i> | <i>d</i> ,<br>Å | $\sin^2 \theta$<br>(Observed) | $\sin^2 \theta$<br>(Computed) | Intensity<br>(Observed) | Relative<br>Intensity<br>(Computed) |
|------------|-----------------|-------------------------------|-------------------------------|-------------------------|-------------------------------------|
| 110*       |                 |                               | 0.0543                        |                         | 21                                  |
| 200        | 2.34            | 0.1079                        | 0.1086                        | m                       | 425                                 |
| 210        | 2.08            | 0.1366                        | 0.1357                        | s                       | 1000                                |
| 211        | 1.90            | 0.1637                        | 0.1628                        | s                       | 880                                 |
| 220*       |                 |                               | 0.2171                        |                         | 3                                   |
| 310*       |                 |                               | 0.2714                        |                         | 6                                   |
| 222        | 1.349           | 0.3262                        | 0.3257                        | vw                      | 58                                  |
| 320        | 1.296           | 0.3534                        | 0.3528                        | w                       | 195                                 |
| 321        | 1.247           | 0.3818                        | 0.3800                        | m                       | 430                                 |
| 400        | 1.165           | 0.4369                        | 0.4342                        | w                       | 145                                 |
| 411-330    |                 |                               | 0.4885                        |                         | 2                                   |
| 420        | 1.044           | 0.5442                        | 0.5428                        | w                       | 130                                 |
| 421        | 1.019           | 0.5714                        | 0.5699                        | vw                      | 53                                  |
| 332        | 0.9962          | 0.5978                        | 0.5971                        | w                       | 125                                 |
| 422        |                 |                               | 0.6514                        |                         | 1                                   |
| 510-431    |                 |                               | 0.7056                        |                         | 3                                   |
| 520-432    | 0.8686          | 0.7864                        | 0.7871                        | m                       | 320                                 |
| 521        | 0.8535          | 0.8143                        | 0.8142                        | m                       | 290                                 |
| 440        | 0.8266          | 0.8683                        | 0.8685                        | m                       | 300                                 |

Quadratic form for copper K $\alpha$  radiation:

$$\sin^2 \theta = 0.02714 (h^2 + k^2 + l^2)$$

s = strong; m = medium; w = weak; vw = very weak.

\* Reflection observed in a pattern obtained with chromium K $\alpha$  radiation.

each cobalt atom is surrounded by twelve vanadium atoms at 2.61Å; each vanadium atom is surrounded by two vanadium atoms at 2.34Å, four cobalt atoms at 2.61Å, and eight vanadium atoms at 2.86Å.

## Acknowledgment

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TN 79E. Manuscript, March 5, 1951.



## Twenty-Five More Years of Metallography

by J. R. Vilella

IN accordance with the custom of this society, we are gathered here, as we have every year since 1924, to honor the memory of the eminent American metallurgist and teacher, Professor Henry Marion Howe. Unlike many of the distinguished metallurgists who have preceded me as a Howe lecturer, I cannot bring to you reminiscences of his personality, for it was not my privilege to be associated with Professor Howe, or to be directly one of his students. Yet, Professor Howe and Professor Albert Sauveur, through the medium of their books, were my first teachers of metallography, as they have been of almost all American metallurgists of my generation. As a teacher, and for many years the acknowledged leader of American metallurgists, he exercised a profound influence in the growth of our science and was held in honor by the men of science of his time. I can speak no words of technical appreciation that will add luster to his fame, for by his prophetic vision, his teachings, and his researches he stands among the immortals in the memory of all metallurgists.

In 1926, the third Howe Memorial Lecture was presented by Professor William Campbell<sup>1</sup> of Columbia University, who entitled it "Twenty-Five Years of Metallography." He took as a starting date for his chronology the turn of the century, which coincided with his arrival from England to work in association with Howe at the Columbia School of Mines. In that informative lecture Professor Campbell enumerated the important advances in metallography achieved during the first quarter of the century, and, it now appears, may have established the custom of reviewing such progress every twenty-five years. The scope of Professor Campbell's lecture was as broad as his metallurgical knowledge, for it embraced a wide portion of the field of metallography, both ferrous and nonferrous.

Twenty-five years later, the Howe Memorial Lecture Committee saw fit to assign to me the honor of writing a lecture that would commemorate the work of Henry Marion Howe and would at the same time constitute the 25th anniversary of the lecture by Professor Campbell. The Committee suggested that this lecture might properly be called "Twenty-Five More Years of Metallography," a suggestion that I

have adopted. I must confess, however, that I have not followed the precedent established by Campbell and have narrowed the scope of this lecture to an appraisal of those achievements which in my opinion have contributed most to the progress of microscopical metallography during the past twenty-five years.

### Progress in Metallography

The metallographic methods most widely used today, with the exception of the electron microscope, were firmly established more than twenty-five years ago. In general, our specimens were prepared for microscopic examination in those days in much the same manner as they are today. It is true that new details of technique have been introduced from time to time, and that superior equipment is available today, but on the whole, these improvements have been in the nature of refinements, often a matter of personal preference, and none can be considered essential to the attainment of the ultimate goal of the art and science of metallography, which is to reveal the structure of metallic specimens with unequivocal clarity so that they may be interpreted correctly.

Mechanical metallographic polishing, which was the only method available in 1926, is still universally practiced and still consists of abrading the metallic specimen with a series of abrasives of increasing fineness until a specular surface is attained. We have now the alternative method of electropolishing, but it is not widely used because, except in a few special cases, its results are inferior to those of competent mechanical polishing.

Likewise, most of the etching reagents preferred today were in common use more than twenty-five years ago and were applied in the same manner as they are today. Valuable improvements have been made in the optical and mechanical performance of metallurgical microscopes, but there was no dearth in those days of excellent instruments equipped with achromatic and apochromatic objectives capable of yielding micrographs comparable in quality with the best that we can make today. In fact, it would be a difficult task for any metallographer today to make optical micrographs at magnifications in excess of 3000 diameters that would surpass those made by Lucas more than twenty-five years ago. One of these is shown in Fig. 1. Yet, it is unquestionable that on the whole, the micrographs appearing in the metallurgical literature today are vastly superior to those

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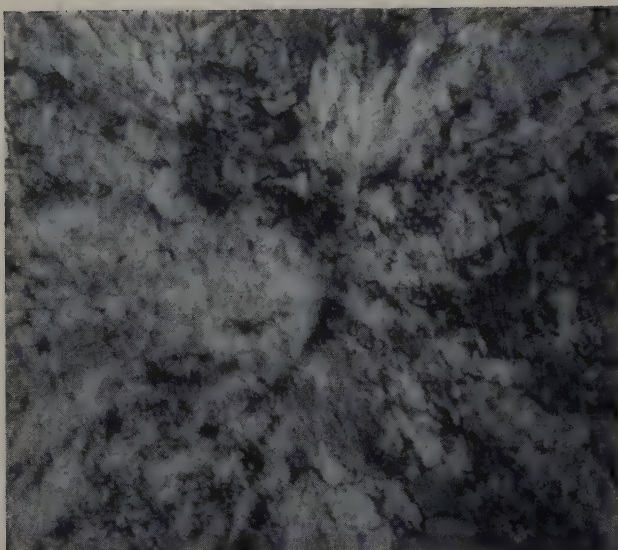


Fig. 1—Partly resolved nodule of fine pearlite. Made by F. F. Lucas prior to 1926. X3650.

of twenty-five years ago. Since progress in metallography is best reflected in the quality of the published micrographs, it suffices to compare those used as illustrations in the volume of the *Transactions* of this Institute which contains the Howe Memorial Lecture of Professor Campbell<sup>1</sup> with those illustrating any recent volume, to appreciate the magnitude of the progress accomplished during the past twenty-five years. But since this notable progress does not stem from new techniques or superior equipment, what brought it about? I believe it is the inevitable consequence of a better concept of what constitutes a properly prepared metallographic specimen. The aim of the metallographer some years ago was the attainment of a highly specular surface of adequate flatness, free from scratches. At the cost of many errors of interpretation and much confusion in our concept of some of the structures of steel, we have learned that these requisites are not enough; that in addition the nonmetallic inclusions have to be preserved intact so that the cleanliness of the steel may be judged correctly, and most important of all, that the polished surface has to be freed from all traces of flowed or disturbed metal before the true struc-

ture of the metal can be seen. Rapid progress began when the idea spread among metallographers that the structure observed in specimens which had been polished and etched just once, was seldom the true structure of the metal. The fact that a polished metallic surface owed its specular finish to a layer of flowed metal had long been known, but the effect of incomplete removal of this layer on the appearance of the structures of steel and other metals was not appreciated. In fact, it was generally assumed that this layer of flowed, or amorphous metal, as it used to be called, was removed completely during the first etching and therefore very few questioned the authenticity of a structure revealed in a sample polished by a competent operator and etched in one of the standard reagents. It is my belief that our failure to rid the surface of metallographic specimens of this insidious layer of disturbed metal was one of the most subtle but effective obstacles blocking progress in our knowledge of the structures of steel and that it entailed consequences from which metallography has but recently recovered.

We need only to recall our concepts of some of the structures of steel prevalent about 1926, and the nomenclature and phraseology that grew logically out of those concepts, to appreciate how greatly our ideas have changed since it became possible to see the true configuration of the structures of steel. It was then generally agreed that pearlite was the structure resulting from direct transformation of austenite and exhibiting alternate lamellae of ferrite and carbide, Fig. 2. Martensite was universally recognized as the slow-etching acicular structure of great hardness resulting from low temperature transformation of austenite and generally obtained by cooling steel rapidly from the austenitizing temperature, Fig. 3. Likewise, there was no hesitancy in identifying as troostite, the dark etching, nodular structure often found associated with martensite in rapidly cooled steels, Fig. 4. In the high carbon alloys there was no difficulty in identifying ledeburite or proeutectoid cementite occurring either as a massive network or as primary needles. These are illustrated in Figs. 5 and 6 respectively. Mixtures of martensite and retained austenite, such as illustrated in Fig. 7, were likewise readily recognized in very high carbon steels. However, if the structure observed under the microscope was a dark-

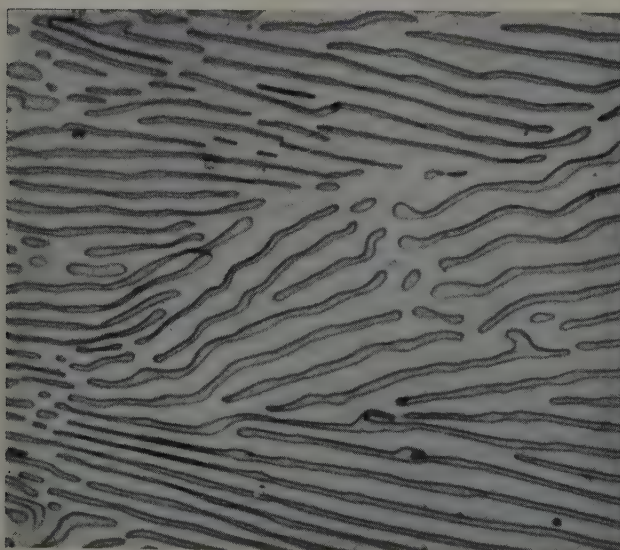


Fig. 2 (left)—Pearlite 0.89 pct C steel transformed isothermally at 1325°F. X2500.  
Fig. 3 (right)—Martensite 0.87 pct C steel water quenched. X1000.



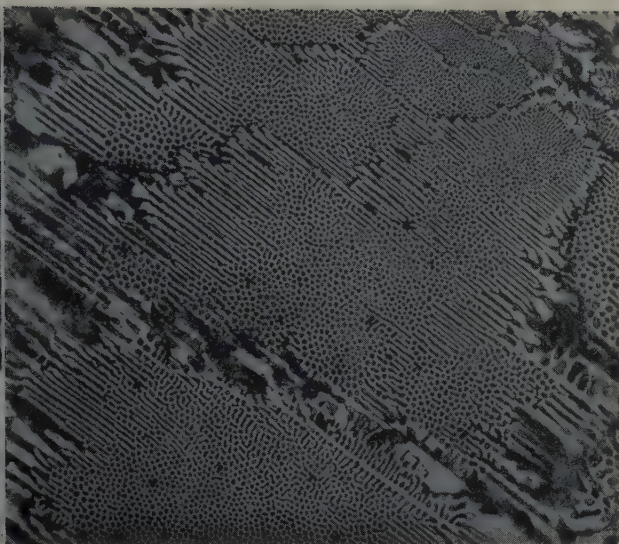
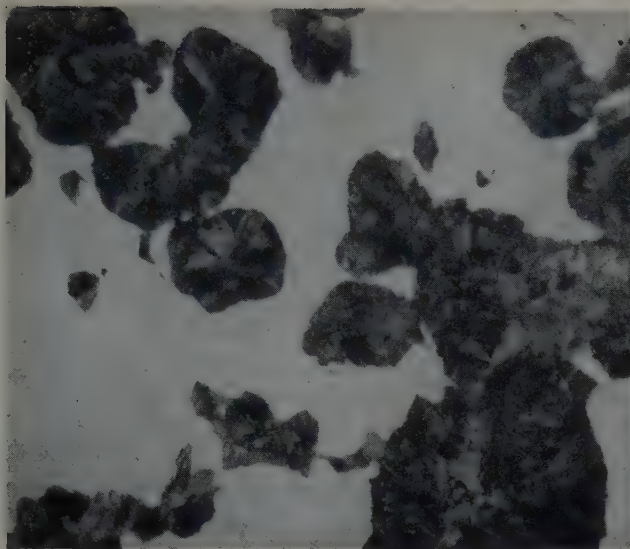


Fig. 4 (left)—Nodular fine pearlite (troostite) 0.89 pct C steel water quenched. X750.

Fig. 5 (right)—Ledeburite 3 pct Cr steel melted in a graphite crucible. X150.

etching conglomerate that could not be resolved into lamellae, then the metallurgist had to decide whether it was troostite or sorbite. Since these structures lacked characteristic patterns or configurations on which to base identification, the decision on what to call such a structure depended on the heat treatment that the steel had received. The structure was considered to be troostite if it had been obtained either by tempering martensite at slightly below 750°F or by cooling through the transformation range at a rate slower than that required to form martensite, as for example, by oil quenching, or in the middle of large pieces quenched in water. It was sorbite if produced by tempering martensite between 750° and 1300°F or by air cooling small pieces from the austenitizing temperature. In other words, it was generally accepted that essentially the same structure resulted from the decomposition of austenite on cooling and from the decomposition of martensite on tempering, although by 1926 there was an increasing number of metallurgists who questioned the correctness of that view. We find, for instance, that Professor Campbell in his Howe Memorial Lecture of that year asks, "But have we strong enough evidence to prove that it (troostite) is the same as the secondary troostite that occurs

on cooling?" However, the fact is that the only reason this question had to be asked in 1926 was because, in spite of excellent microscopes and fine apochromatic objectives, we were unable to see that the structures resulting from the direct transformation of austenite were lamellar, whereas those derived from the tempering of martensite were granular. And the reason we could not see this fundamental difference, clearly shown in Figs. 8 and 9, was because our microscopes were focused on a false surface, just a few atomic layers in thickness, over the surface that would have given us a definitive answer. It was our inability to see beyond this false surface, more than any other cause, that gave permanence to the old concepts of sorbite and troostite.

After more than a quarter century of active participation in furthering the art and science of metallography, it is my considered opinion that recognition of the existence of a layer of disturbed metal formed during polishing and its elimination by the practice of alternate polishing and etching, Fig. 10, has been one of the observations that has contributed most to our knowledge of the structures of steel and to the progress of metallography in general. Yet, even after we were able to see clearly, our understanding and proper interpretation of these struc-

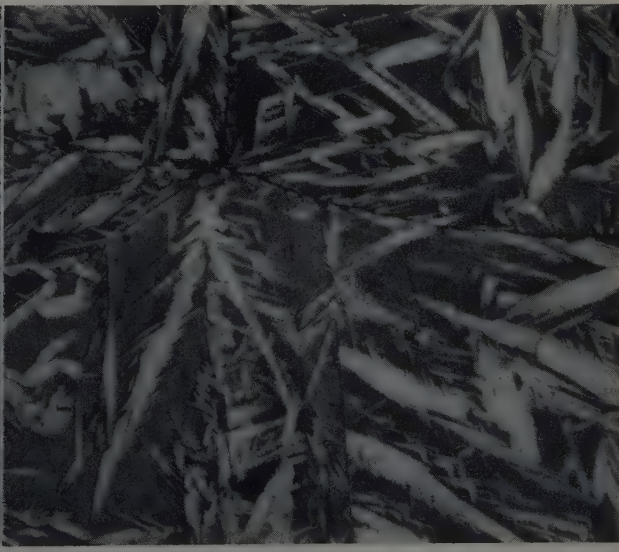
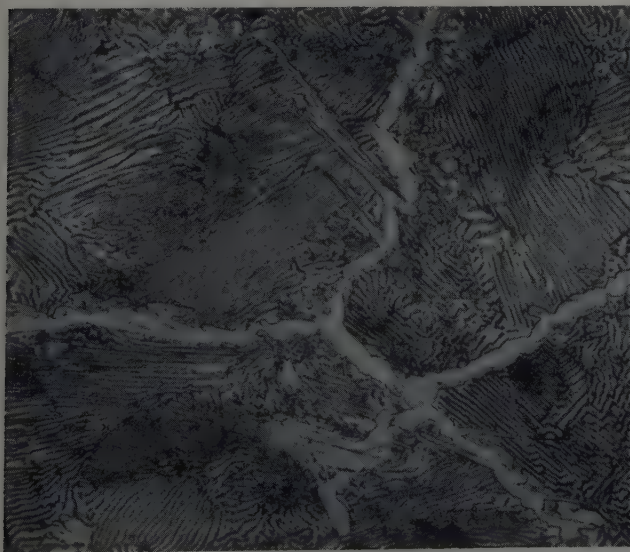


Fig. 6 (left)—Proeutectoid cementite case carburized steel. X2000.

Fig. 7 (right)—Austenite and martensite 1.6 pct C steel water quenched. X500.



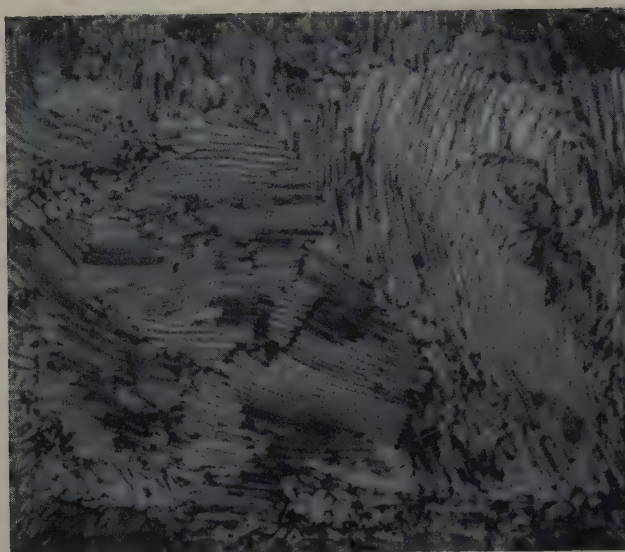


Fig. 8 (left)—Lamellar structure (pearlite) 0.89 pct C steel transformed isothermally at 1225°F. X2500.

Fig. 9 (right)—Granular structure (tempered martensite) 0.87 pct C steel, brine quenched and tempered 1 hr at 1100°F. X2500.

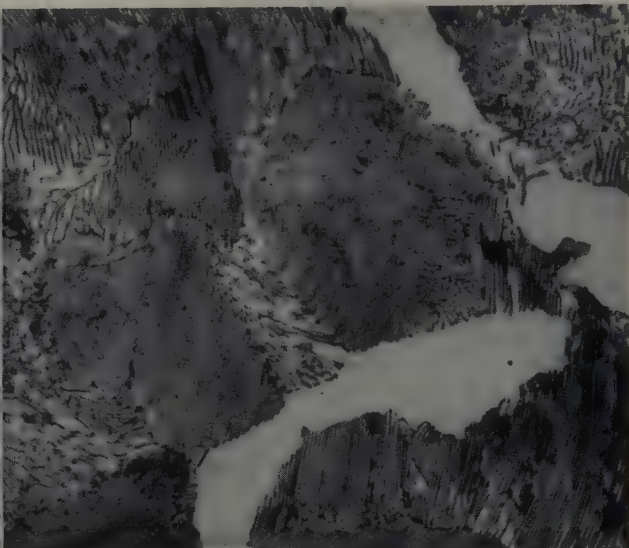
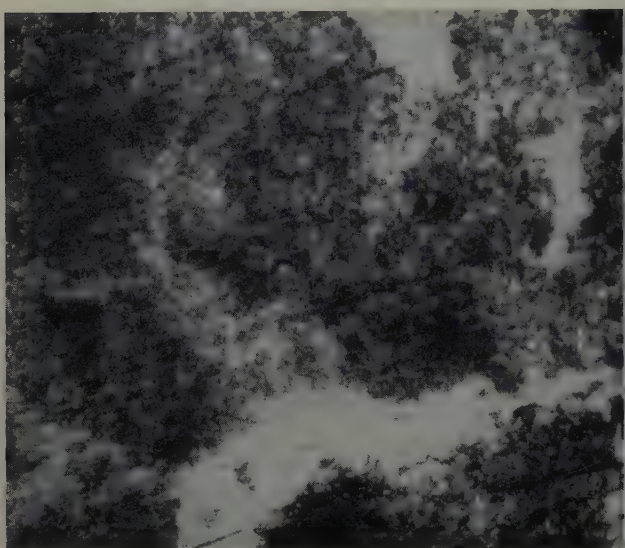


Fig. 10-a (left)—Disturbed metal produced during polishing. b (right)—Disturbed metal eliminated. X1000.

tures might have been delayed had it not been for a contribution from the field of physical metallurgy that I propose to discuss briefly.

This was the investigation by Bain and Davenport into the decomposition of austenite that led to the development of the isothermal transformation diagram. This method of investigation in a comparatively few years turned the emphasis in metallurgical thinking and research from the study of the constitution of alloys after attaining equilibrium at various temperatures to the study of the reactions in solid steel responsible for the aggregate structures, which in turn determine the properties of the alloy. Since the publication of their first paper<sup>8</sup> on the transformation of austenite at constant subcritical temperature in 1930, there have been few major contributions to our knowledge of steel metallography outside of the field of inquiry opened by this epochal work. Its contributions have been in many directions; it established the relation of transformation temperature to type of structure; it enabled us to measure rate of transformation in solid steel; it taught us how alloying elements and variations in austenite grain size exert their influence on hardenability; it disclosed the interrelation of the structures; it gave us a new family of structures, the

bainites, Figs. 11 and 12, whose valuable properties are finding increasing application in diverse industries; it provided us with a scientific basis for revision of the obsolete nomenclature of the structures of steel; and most important of all, it transformed the heat treatment of steel from an art into a science.

In the struggle to rid the metallographic specimen of disturbed metal, the introduction of electropolishing was a welcome aid. For many years we realized that practically every metallographic specimen of austenitic, low carbon stainless steel exhibited striations and figures that were purely a surface condition produced during its preparation. The elimination of these false structures by the technique of alternately polishing and etching, employed with such success in carbon and low alloy steels as well as in nonferrous alloys, proved inadequate when applied to soft austenitic steels. Quite often we were forced to accept the presence of these defects in micrographs intended for publication because we were unable to eradicate them. With the advent of electrolytic polishing this vexatious condition disappeared. If we cannot by ordinary mechanical polishing, we can now by electropolishing, reveal the structure of the softest austenitic al-



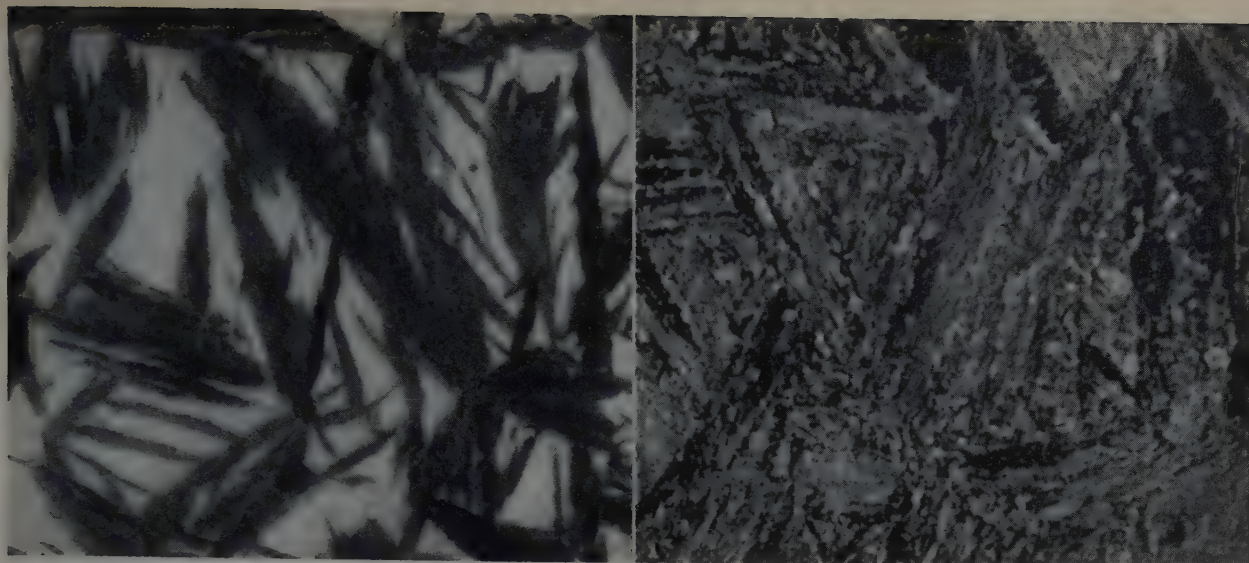


Fig. 11—Bainite 0.89 pct C steel transformed isothermally at 550°F. X2500. a (left)—Partial transformation. b (right)—Complete transformation.

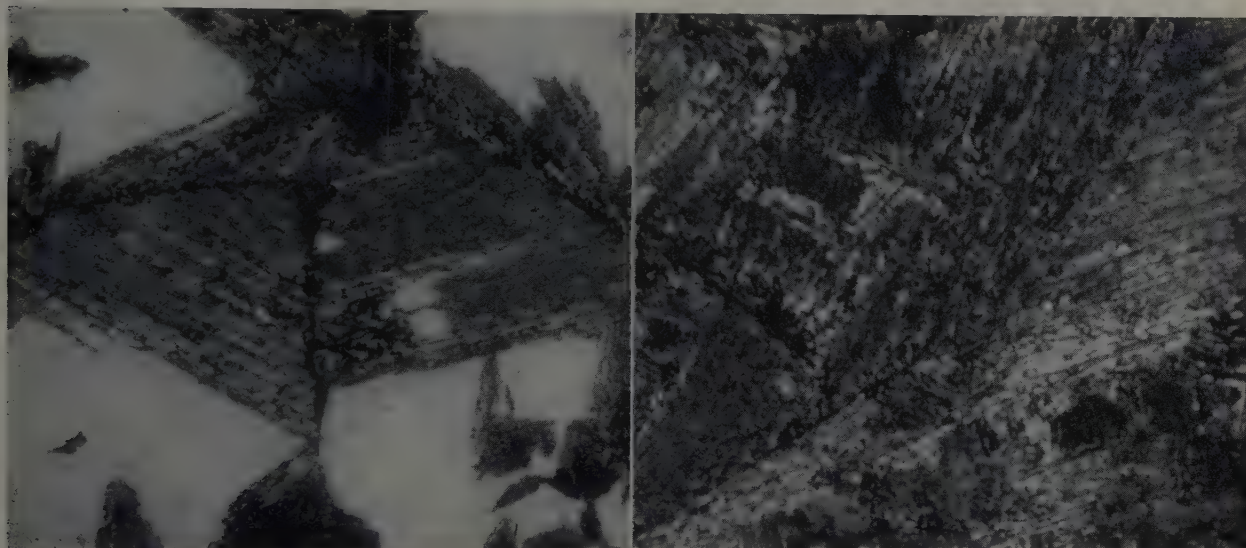


Fig. 12—Bainite 0.89 pct C steel transformed isothermally at 850°F. X2500. a (left)—Partial transformation. b (right)—Complete transformation.

loys free from confusing artifacts, as may be seen in Figs. 13 and 14. Unfortunately when electropolishing is applied to steels other than the stainless grades, it often results in excessive pitting of the nonmetallic inclusions and for this reason we do not often encounter in the literature micrographs made from electropolished surfaces. However, the method is finding increasing application in the preparation of specimens intended for routine examination at low power, and may lead, by simplifying their preparation, to more frequent use of the microscope as a tool of routine inspection.

Not many years ago a micrograph was considered satisfactory if the structure photographed was recognizable. Such defects as uneven illumination, pits resulting from dislodgement of nonmetallic inclusions, excessive or insufficient contrast, or incomplete removal of disturbed metal were all too common. Today any of these defects is deemed intolerable by an increasing number of metallographers. The excellence of the micrographs entered in competition every year at the American Society for Metals and other metallurgical conventions attest to the craftsmanship of many of our younger metallographers and to the pride they feel in achieving a beautiful photographic representation

of a structure. Yet, careful examination of these selected micrographs often reveal deficiencies directly traceable to inability of the metallographers to make proper use of the adjustments and associated apparatus provided by the manufacturer of microscopes for improvement of the image. Such deficiencies, small as they are in contrast with the gross defects of years past, are nevertheless a glaring reflection of shortcomings in the training of metallographers. The microscope is their all-important tool, but because they are not always conversant with the principles of optics underlying the instrument, they often fail to utilize its full potentialities. They are expected to produce a faithful photographic reproduction of a microstructure, but they have not been trained in the art and science of photography sufficiently to use this very flexible process with skill and artistry. There is probably no greater contribution that our colleges can make toward future progress in the art of metallography than to stress the teaching of the fundamental principles of microscopy and of photography.

### The Electron Microscope

Ever since the introduction of the electron microscope metallurgists have believed that the great



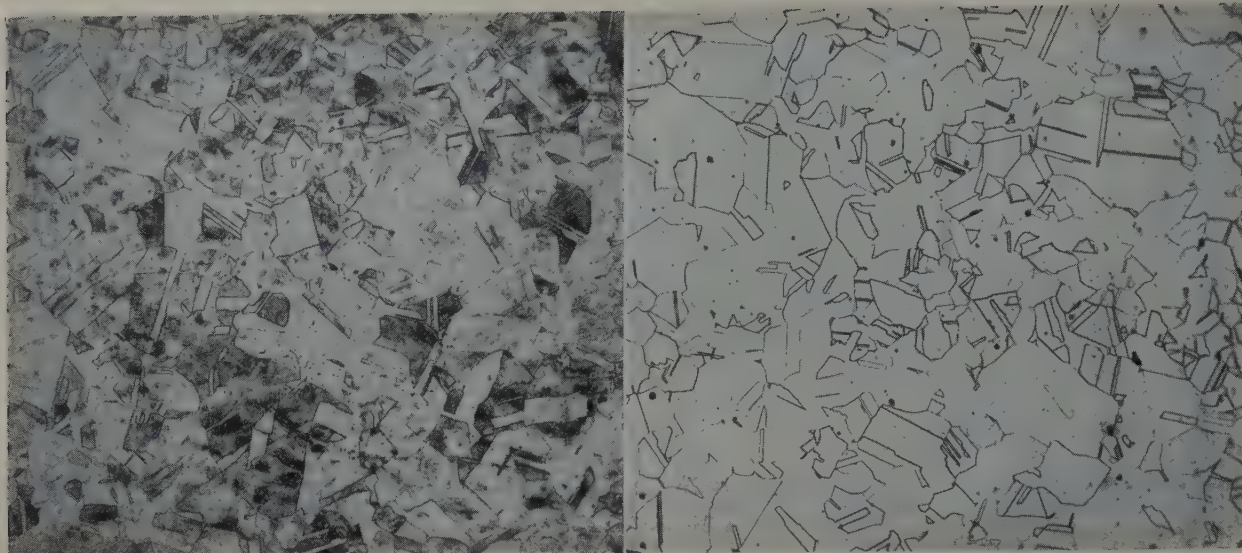


Fig. 13—18-8 stainless steel. X100. a (left)—Polished mechanically. b (right)—Polished electrolytically.

resolving and magnifying power of this instrument would be of inestimable value in exploring the fine microstructures of steel and in the study of metallurgical processes involving precipitation of constituents too fine for resolution with the optical microscope. The first attempt in this direction demonstrated the ability of the microscope to resolve significant details beyond the limits of the optical instrument, but it was immediately apparent from the markedly dissimilar results obtained by different investigators that before its inherent advantages could be realized the causes leading to such diversity of results had to be ascertained and eliminated.

It was the consensus of a group of electron microscopists and metallurgists that by concerted study of the various steps involved in the production of an electron micrograph it should be possible to arrive at a degree of standardization of procedure that would result in satisfactory agreement between different investigators as to the appearance of presumably similar structures. To accomplish this purpose the Joint Committee on Electron Microstructures of Steel was organized in 1948 and a program of investigation formulated, consisting of heat treating a series of pieces of eutectoid steel and dividing these pieces into specimens which were supplied, together with a high-power optical micrograph of each structure, to each of the cooperating laboratories for study with the electron microscope. In 1949 this group became affiliated with Committee E4 on Metallography of the American Society for Testing Materials and in 1950 the first progress report of this work was published. It is this report that I wish to review today because in my estimation it represents a contribution to our knowledge of the structures of steel.

Paraphrasing the conclusion and summary of this report, the work of this Committee demonstrates, first of all, that high fidelity electron micrographs of the structures of steel can be obtained by present-day replica techniques. This is evidenced particularly by the close similarity in appearance between light and electron micrographs of such structures as pearlite and spheroidized carbides which, because of their relative coarseness, can be well resolved with the optical microscope, see Fig. 15.

Inasmuch as these micrographs leave little doubt that faithful reproductions can be made by the

replica technique of electron metallography, our confidence is greatly strengthened in the ability of the method to show us the true appearance of those structures that are too fine for adequate resolution with the optical microscope. Likewise, there should be little hesitancy in the use of electron micrographs for measurement of structural dimension, whenever such measurements are desired.

Considering some of the fine structures of steel, we see in Fig. 16 that the structure resulting from the transformation of austenite in the vicinity of the nose of the isothermal transformation diagram, which for years we had inferred was finely laminated pearlite, is actually just that.

It will not be possible to present all the micrographs contained in this report but it would be remiss to omit those that can teach us something. For example, the microstructure of bainite formed at 750°F, shown in Fig. 17, appears to have been completely resolved and found to consist of discrete, chunky cementite platelets, more or less randomly distributed and oriented in the ferrite matrix. The length of these platelets is estimated to vary between 600 and 1000Å, with the larger size predominating.

Fig. 18 indicates that the structure of bainite obtained by isothermal transformation at 500°F consists of ferrite bands containing cementite platelets in parallel array.

No definite fine structure is identifiable in the needles of untempered martensite, as may be seen in Fig. 19, but the sharp definition of even very small areas of retained austenite suggests that the electron microscope would be of value in improving the accuracy of quantitative estimations of retained austenite.

While attention is focused on Fig. 19 exhibiting comparatively soft austenite in hard martensite, permit me a brief digression to point out that all these micrographs were obtained from surfaces polished as for optical metallography, yet, in spite of the high resolution and magnification of the electron microscope, no scratches or other imperfections attributable to mechanical polishing are detectable. This is significant because it attests to the adequacy of the technique of polishing on which optical metallography has always depended. Likewise, since our concept of the appearance of the structures of steel has been based on the use of



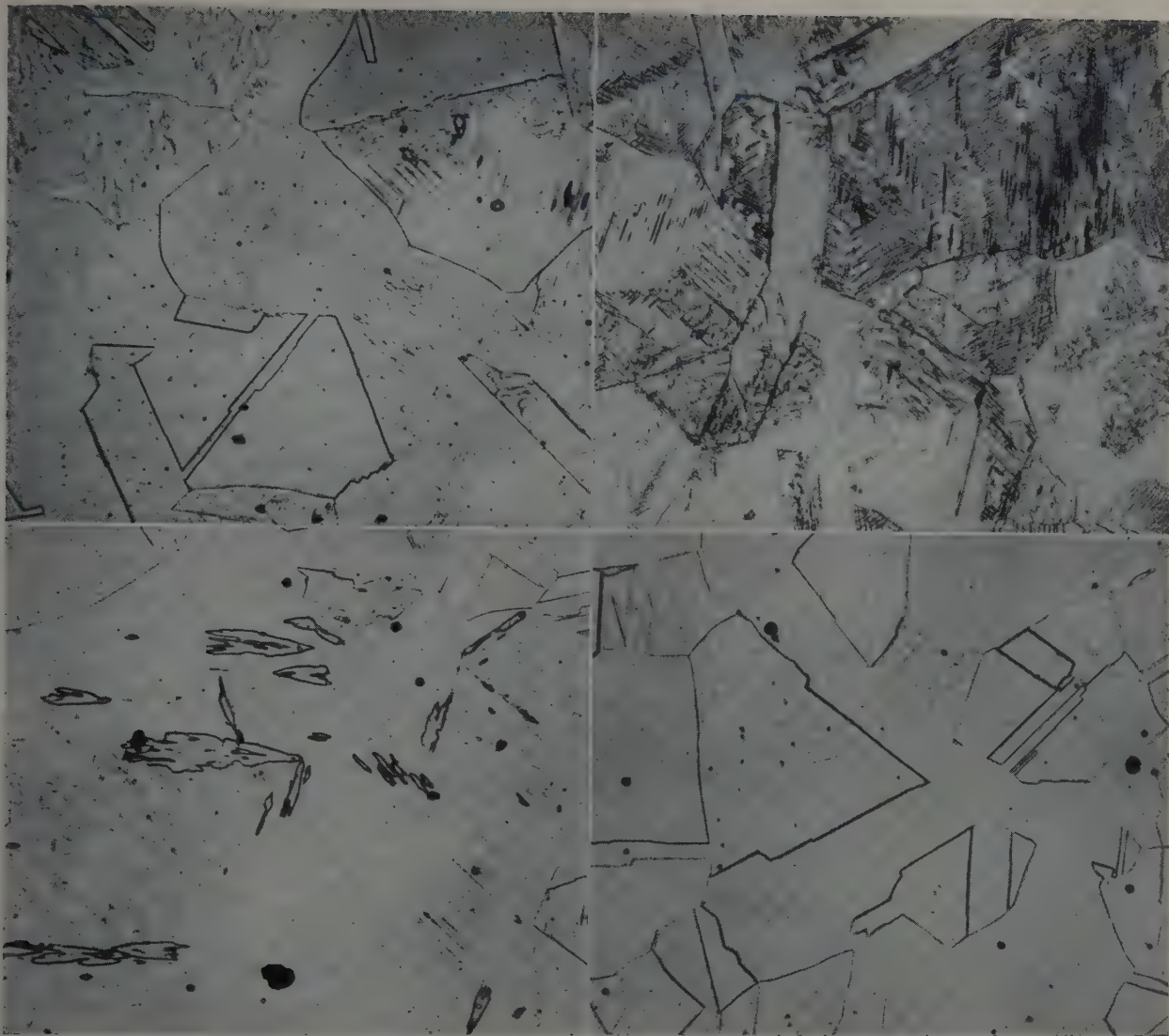


Fig. 14—18-8 stainless steel. a (upper left), b (upper right), and c (lower left) are false structures produced during mechanical polishing. d (lower right) is the true structure obtained by electrolytic polishing. X500.

pical and nital as etching reagents, it is indeed fortunate that these solutions have been found equally satisfactory for electron metallography.

The structure of martensite tempered at 400°F, illustrated in Fig. 20, is of particular interest for two reasons; first, because it shows that the precipitate responsible for the dark-etching characteristic of this structure is of such extreme fineness as to tax even the resolving power of the electron microscope, and second, because the areas of untransformed retained austenite so clearly shown in the optical micrographs are not identifiable in the electron picture.

Since, according to the isothermal transformation diagram for this steel, a considerable amount of the original retained austenite should remain untransformed after tempering 1 hr at 400°F, our inability to identify it in the electron micrograph can only be interpreted as a failure of the method to reveal clearly the true structure of the specimen. X-ray analysis shows that this specimen contains 9 pct of retained austenite.

Likewise, the optical micrograph and X-ray analysis of the specimen tempered 1 hr at 800°F, Fig. 21, indicates the disappearance of the last traces of retained austenite, which must have transformed isothermally to 800°F bainite during tempering, yet in the electron micrograph, martensite tempered at

800°F cannot be differentiated from bainite formed at the same temperature.

In calling attention to the apparent failures of the electron microscope to reveal subtle differences in the structure of steel my only purpose has been to emphasize my opinion that further refinements of technique are necessary before the full potentialities of this instrument are realized.

### Microscopes

The first step in the development of the modern metallurgical microscope dates back to 1872 in Vienna, when V. von Lang<sup>3</sup> first fitted a microscope with a plain glass vertical illuminator in order to examine opaque objects. This was followed in 1897 by Le Chatelier's<sup>4</sup> design of an inverted instrument that made it possible, by merely placing the specimen on the stage, polished surface down, to attain the necessary perpendicularity to the optical axis. By 1926 this design had been adopted by the leading manufacturers of microscopes, and inverted instruments equipped with plain glass vertical illuminators had become standard equipment of the metallurgical laboratory. Numerous mechanical improvements and refinements, some of them marvelously ingenious, have been made in recent years and the versatility of the instrument has been increased many fold by the addition of several more or less



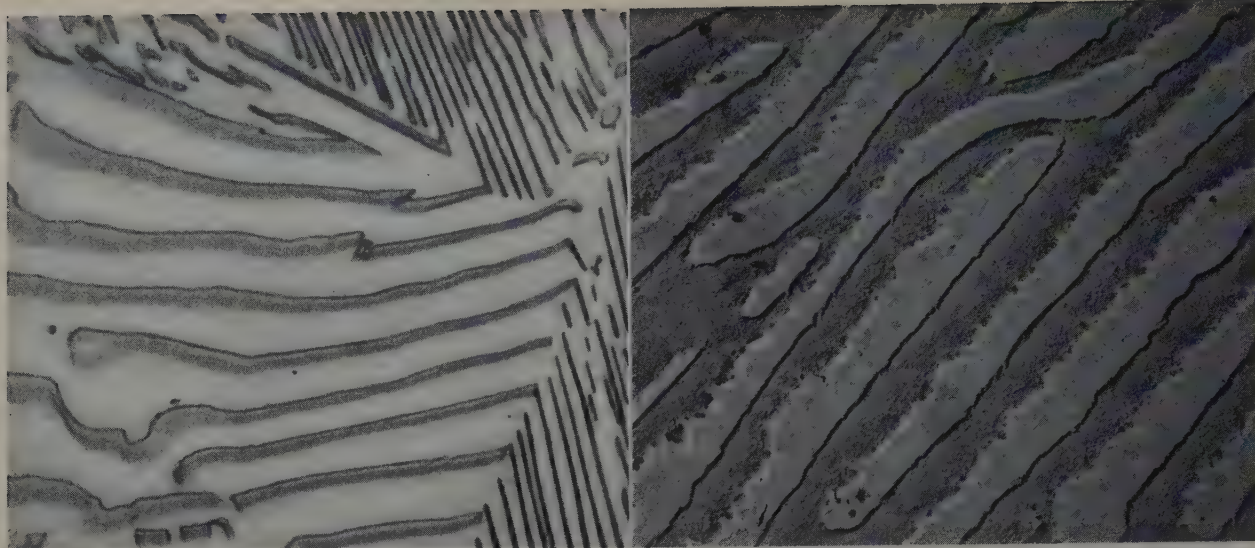


Fig. 15—Pearlite 0.87 pct C steel transformed isothermally at 1300°F. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.

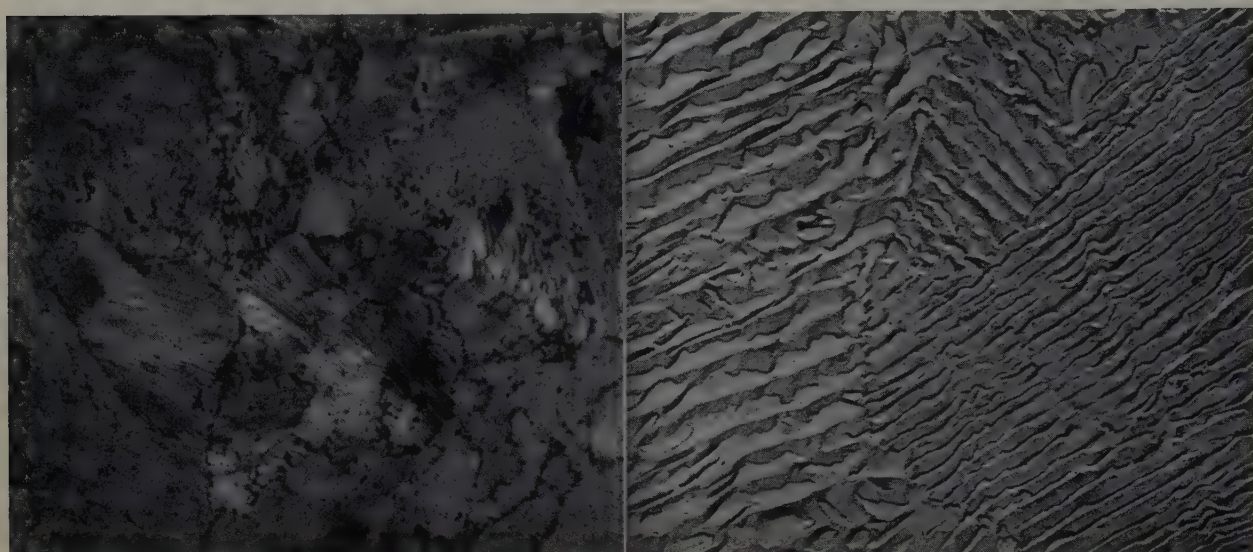


Fig. 16—Fine pearlite 0.87 pct C steel transformed isothermally at 1100°F. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.

useful attachments and accessories. It is the merits of these supplementary accessories that I propose to discuss now.

The first of these, and in my estimation the most valuable, was so-called conical illumination invented by Harry S. George,<sup>5</sup> then with the Union Carbide and Carbon Research Laboratories. The invention was made about 1922 but it was not incorporated into metallurgical microscopes until after 1926. With this simple but effective device it became possible to cut off from the illuminating pencil of light the central, more or less parallel rays, and by utilizing only inclined rays, to illuminate the specimen obliquely, thereby creating highlights and shadows that reveal with stereoscopic realism the three dimensions always present in polished and etched metallic surfaces.

While the geometric exactitude of a micrograph made with axial illumination may be unimpeachable, it is not a truly "natural" representation of the structure and sometimes it is not a satisfactory one. An image or a micrograph lacking such gradations of light and shadow as are encountered in objects illuminated by oblique light is little more than a drawing of a two dimensional pattern, or a map of

the structure in which elevations and depressions are not identifiable. Such representation of the structure is likely to be deficient technically as well as aesthetically, for in many structures significant detail is often not visible except when the highlights and shadows created by oblique lighting bring it out in relief. (See Figs. 22 and 23.)

Unfortunately, the very virtue of conical illumination by which it brings out hidden details and enables us to see the natural contours of a structure, discourages its use, for it also placed in bold relief polishing imperfections which the metallographer would rather not emphasize. But although micrographs made under conical illumination do not appear in the metallurgical literature as frequently as they deserve, conical illumination is nevertheless the most nearly indispensable of the supplementary accessories, for the need of knowing whether a constituent is in relief or in intaglio arises during a metallographic examination more often than the need to examine the structure under polarized light, dark field illumination, or phase contrast.

In addition to conical illumination, the modern, up-to-date, metallurgical microscope is equipped for viewing the specimen under polarized light,



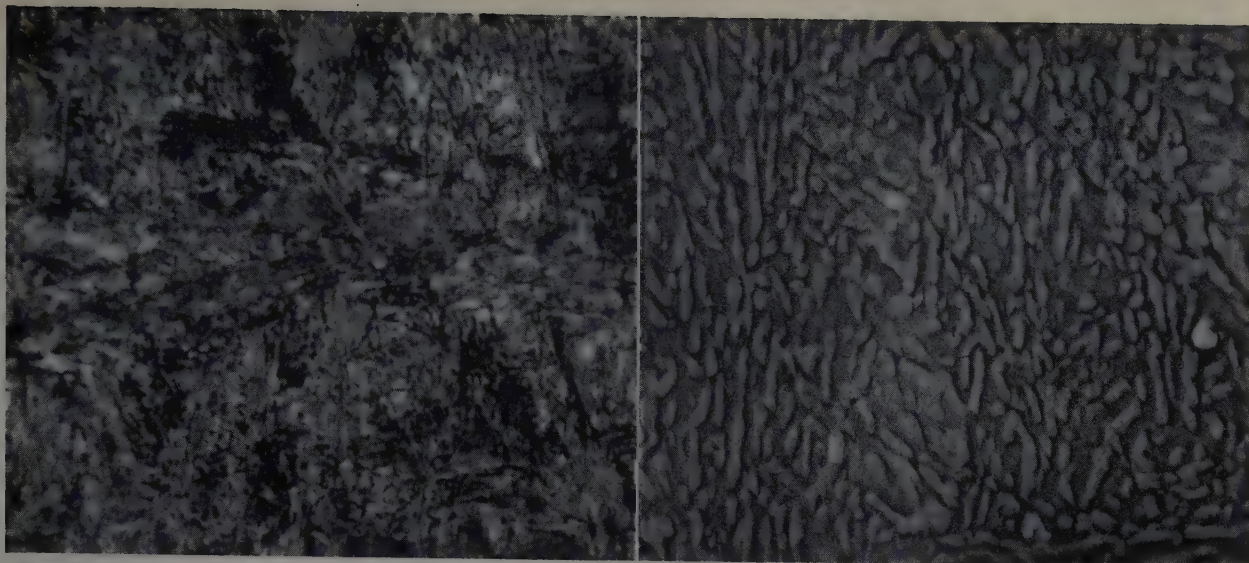


Fig. 17—Bainite 0.87 pct C steel transformed isothermally at 750°F. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.

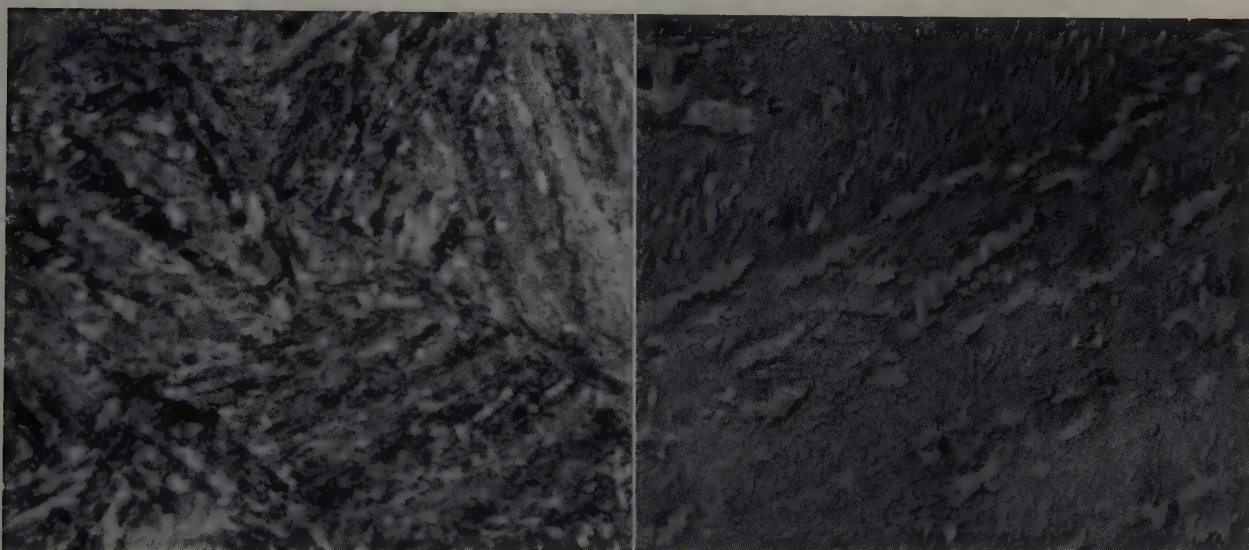


Fig. 18—Bainite 0.87 pct C steel transformed isothermally at 500°F. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.

dark field and phase contrast illumination. Each of these systems of illumination contributes from time to time valuable items of information and their place in the metallurgical microscope is justified, but to date their contributions to our knowledge of the structure of steel have been decidedly minor.

Examination of unetched surfaces with reflected polarized light under crossed Nicols sometimes enables the metallographer to distinguish between inclusions having isotropic and anisotropic properties, and these characteristics together with the color reflected through transparent inclusions from the metal-inclusion interface, sometimes helps in identifying the inclusion. The vitreous character of some globular nonmetallic inclusions has been shown by the appearance of a dark optical cross when examined under crossed Nicols. Several investigators have made use of reflected polarized light in the identification of constituents, such as sigma phase in iron-chromium alloys; others to delineate grains in martensite, but these applications have been few and as yet the value of the method in the identification of constituents has not been proven.

The contribution of dark field illumination has been primarily to enhance contrast when such en-

hancement was deemed desirable. This enables one to see clearly grain boundaries and other details of structures not readily visible under bright field illumination because of insufficient contrast. Professor Desch<sup>6</sup> finds it particularly useful in the examination of deeply etched or pitted specimens, as when studying surface corrosion. He reports that, "pits which appear under vertical illumination merely as black spots may be examined in detail, the color or form of the corrosion product contained in them being clearly seen." At low power, when the depth of field is considerable, it is very useful in examining unpolished surfaces, for it reveals the colors of the specimen with greater brilliancy and fidelity than with any other form of illumination.

#### Phase Contrast

Another optical accessory recently made available for incorporation into the metallurgical microscope is an attachment for illuminating the specimen under the conditions known as phase-contrast. The theory and graphic representation of this system of illumination is too involved for presentation in a paper of this type, but the following may give an idea of its potential usefulness to metallography.



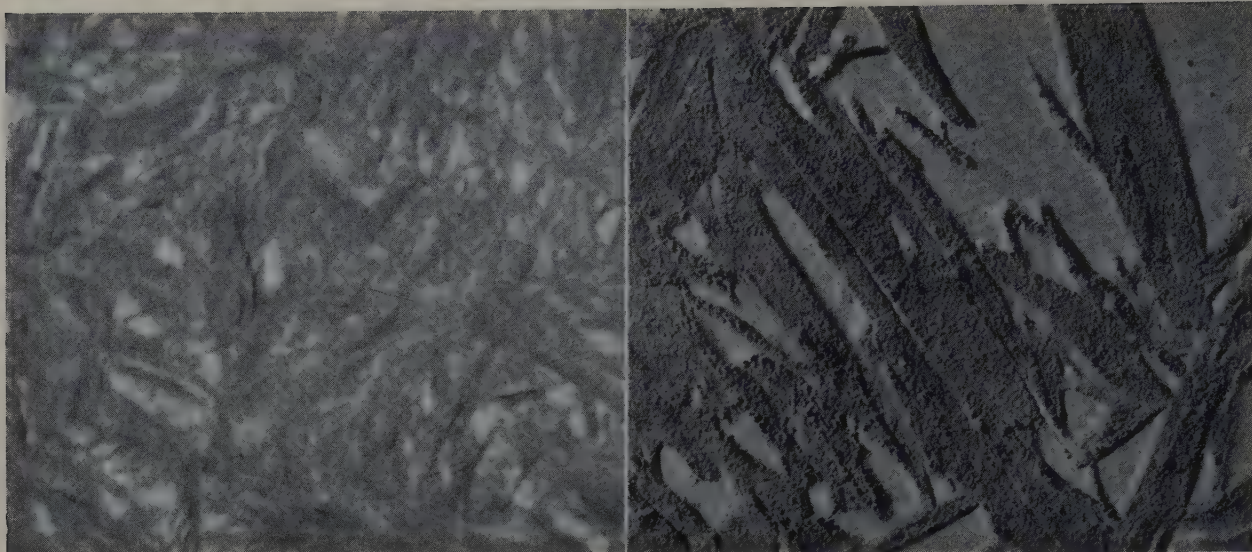


Fig. 19—Martensite and retained austenite 0.87 pct C steel water quenched. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.

The distribution of brightness throughout an image as we see it with an ordinary microscope depends on: 1—relative reflectivity of various parts of the structure, or 2—color differences, or 3—light scattered away from the objective by edges in the structure. It may be noted that it does not depend on differences in level at the surface of the specimen. In other words, two parts of the structure at different levels, their color and reflectivity being equal, will appear equally bright. However, by means of the phase-contrast system of illumination differences in level, which produce differences in the phase of the light reflected from them, are converted into differences in brightness, and hence the term phase-contrast.

It is claimed<sup>7</sup> that by this means it is possible to show differences in level of the order of 50Å (approximately 20 interatomic distances) and there is no question that for this purpose the method has great sensitivity, but as yet we do not know what use to make of the information supplied by this sensitive, ingenious method. It is also claimed that phase-contrast is sensitive to differences in surface material,<sup>8</sup> a claim that your speaker was unable to substantiate during his limited experience with this system of illumination. However, if this claim is

found to be valid and incident phase-contrast can be employed to differentiate constituents which under ordinary illumination appear identical, then regardless of the usefulness of data pertaining to differences in level, the method will become a valued tool of metallography.

The contribution of phase-contrast illumination to our knowledge of the structure of steel to date has not been significant, but the tool has been available to metallographers for a short time and it would be premature to pass judgment on its eventual merit.

#### Coated Lenses

A development in the manufacture of photographic lenses which in recent years has aroused considerable interest and which, when extended to microscope objectives and eyepieces, led to a marked improvement of the image, is the anti-reflection coating applied to glass-air interfaces in order to decrease internal reflections, or flare.

In a metallurgical microscope the objective acts first as condenser to illuminate a portion of the polished surface and then as a lens to form an image of the illuminated field: Thus the opportunity for reflections are double those of a microscope used with transmitted light, and consequently, excessive

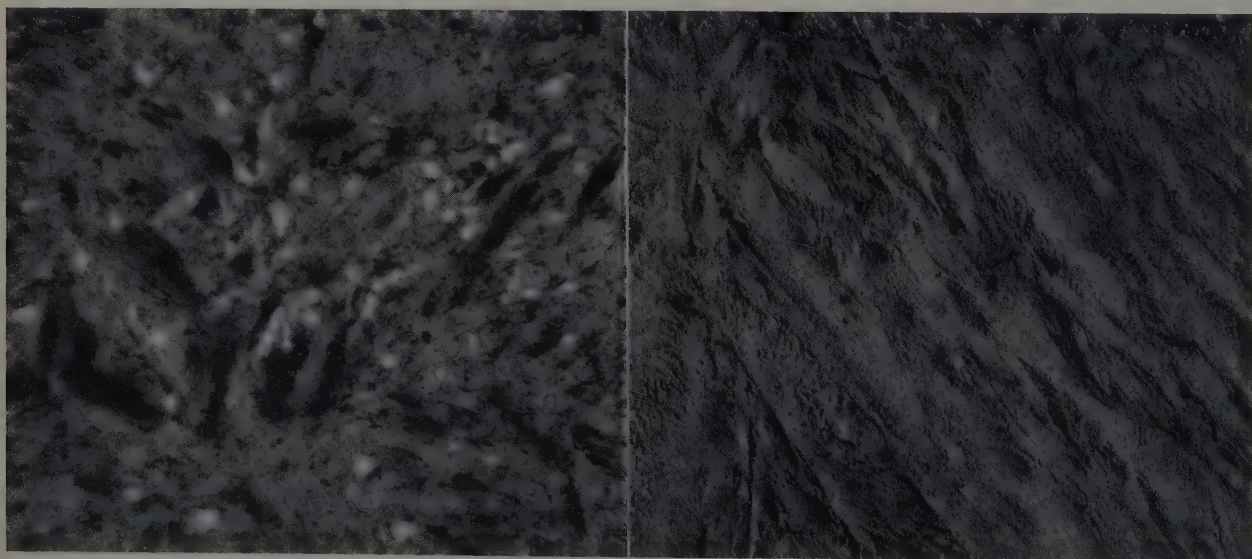


Fig. 20—Tempered martensite 0.87 pct C steel quenched in water and tempered 1 hr at 400°F. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.



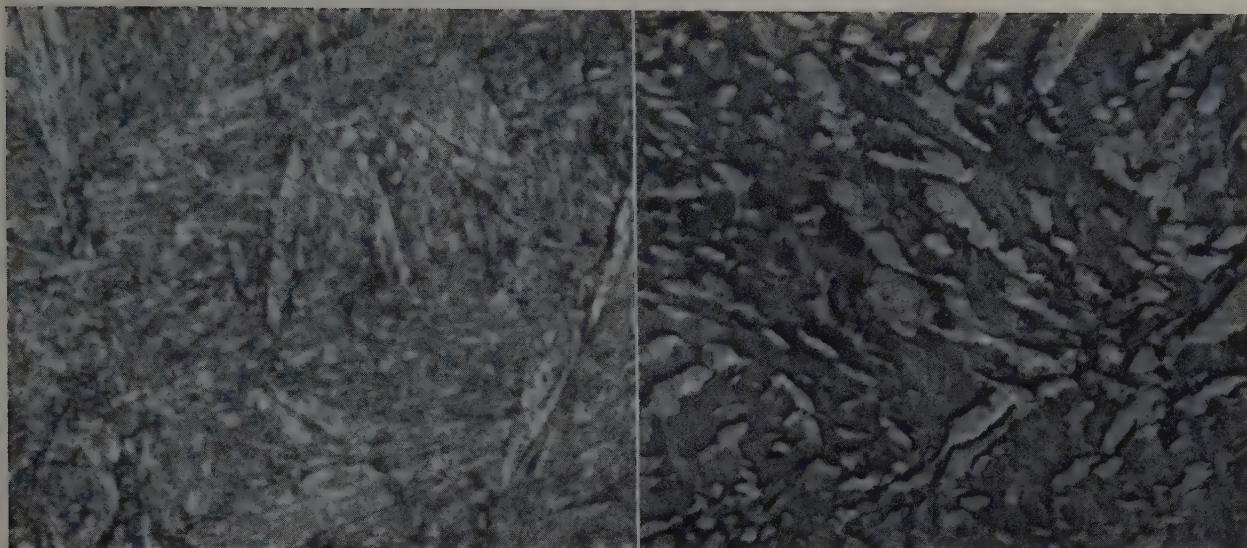


Fig. 21—Tempered martensite 0.87 pct C steel quenched in water and tempered 1 hr at 800°F. a (left)—Light micrograph X2500. b (right)—Electron micrograph X15,000.

internal reflections have been one of the most common and serious defects of objectives designed for metallography. When the illumination is by transmitted light the unwanted reflection is in the direction of the light source and can only reach the image after a second reflection, when its intensity is so low that its effect on the contrast of the image is negligible. On the other hand, when the illumination is by reflected light, the undesirable internal reflection is in the direction of the image and of sufficient intensity to produce a decided veiling effect that impairs seriously the contrast of the image, particularly when the reflectivity of the specimen is low.

To a very considerable extent this defect has been corrected by coating the objective and eyepiece with a transparent film whose thickness is approximately one fourth of the wavelength of the incident light. When the film material is of the correct index of refraction, the light reflected from the glass-film and from the film-air interfaces interfere destructively and only an inconsequential amount of light is then reflected from the surface.

There is another aspect to the application of anti-reflection coating to objectives and eyepieces of great interest to those of us who enjoy making the

best possible micrographs. Since in order to disclose the finest and most delicate details it is necessary to etch lightly, the resulting contrast between the various constituents of the structure is so slight that we are forced to compensate by using photographic plates or films of very high contrast. But since high contrast emulsions are necessarily of slow speed, we have to resort to a strong source of illumination, such as the carbon arc. This is undesirable, for the carbon arc at its best is an unreliable source of the steady, even illumination needed for micrography. The tungsten ribbon filament is definitely preferable, for it gives a steadier and more uniform illumination and is also more convenient to operate, but it cannot always be used, particularly at high magnification, because of insufficient intensity for micrography on slow, high contrast emulsions. But the improvement in contrast brought about by coated optics is sufficiently great to permit the use of faster, lower contrast emulsions and this in turn allows the use of incandescent bulbs. Since the tone range of slow, high contrast emulsions is short, an improvement in tone gradations generally accompanies the use of faster, lower contrast emulsions.

#### Interference Filters

Since not even the finest apochromatic objectives are fully corrected for all colors of the spectrum, it is necessary, if we are to avoid images blurred by residual aberrations, to suppress those wavelengths for which the objective is not corrected completely. For this purpose we employ light filters, mostly in the form of colored glass or gelatin sheets dyed and cemented between glass plates of adequate flatness. The yellow-green filter ordinarily used with achromatic objectives, or the blue-violet often employed to increase the resolving power of apochromats are, in a general way, satisfactory for all but the most exacting metallographic work, but they fall short of performing their intended function ideally since the portion of the spectrum which they transmit is sufficiently wide to include wavelengths for which the objective is not corrected adequately. The ideal filter would be monochromatic, that is, one transmitting only a narrow range of wavelengths in the immediate vicinity of the dominant color. Close approximations to such ideal filters are now available in the form of interference filters.

An interference filter of the transmission type



Fig. 22—Conical illumination. Austenite 1.2 pct C, 6.0 pct Mn steel quenched in brine from 2000°F. X500.



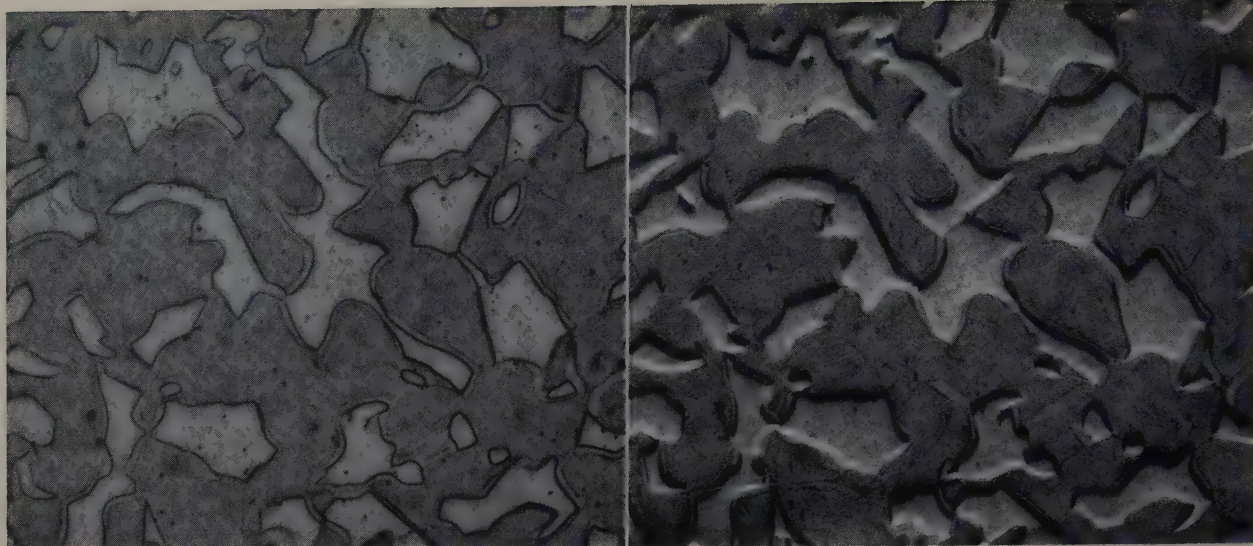


Fig. 23—Conical vs. axial illumination. Ferrite and martensite. a (left)—Axial. b (right)—Conical. X1000.

consists of two semitransparent films of silver separated by one of magnesium fluoride, these three films being deposited on a glass plate with a cemented cover glass for protection. The glass plate and cover glass are not shown in Fig. 24 which is a rather oversimplified schematic representation of the path of a light ray through the filter. The

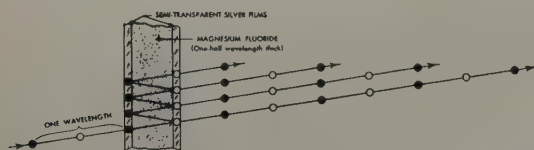


Fig. 24—Path of light through a transmission-type interference filter.

diagram as well as the following description are taken from a Bausch and Lomb publication:<sup>9</sup>

"When the light ray strikes the first silver film part of it is transmitted and passes through the magnesium fluoride coating to the second silver film. Here it is partly reflected and partly transmitted. This process is repeated and this gives rise to multiple reflections between the silver films, and produces a great number of emergent beams. Since the layer of magnesium fluoride is half a wavelength thick and since each doubling back of the light ray forces it to travel twice

this distance, the successive emergent rays are precisely one wavelength apart. When this condition is fulfilled, maximum transmission of light of a particular wavelength occurs and light of other wavelengths is blocked. Consequently the color of the light produced will be determined by the thickness of the coating of magnesium fluoride. In short, the wavelength and, therefore, the color of the emergent light may be precisely controlled; the production of any desired color thus becomes a matter merely of the choice of film thicknesses."

An example of the quality obtained with an interference filter is shown in Fig. 25.

### Color Metallography

Micrography in color is not a development of recent years but dates back probably to 1907 when the Lumiere Autochrome process was introduced commercially. Your speaker made micrographs in color of certain structures in aluminum alloys more than twenty-five years ago. Neither the exposure using a carbon arc nor the development of the plates presented any particular difficulty, and the resulting transparencies were pleasing to look at and accurate as to color rendition. Their main limitation was that when viewed magnified by projection, as in a lantern slide, the colored starch platelets which constituted the color filters of the process, could be seen simultaneously with the image. This granularity reduced somewhat the definition of the finest details of the structure.

With the introduction in more recent years of color films having a high order of resolving power and comparative ease of development in the laboratory, such as Eastman Kodak Ektachrome, or Ansco Color Film, there has been a rebirth of interest in color metallography and some interesting micrographs appear in the literature from time to time. There is no doubt that brilliantly colored subjects are reproduced more faithfully in color transparencies or prints than in black and white and in certain cases the added cost and difficulties inherent in color micrography are fully justified, but one must guard against the temptation of photographing in color for no reason other than making colorful pictures.

In the photographic reproduction of biological subjects where differential staining for purposes of identification is essential, and in metallography when color differences are significant, micrography in color

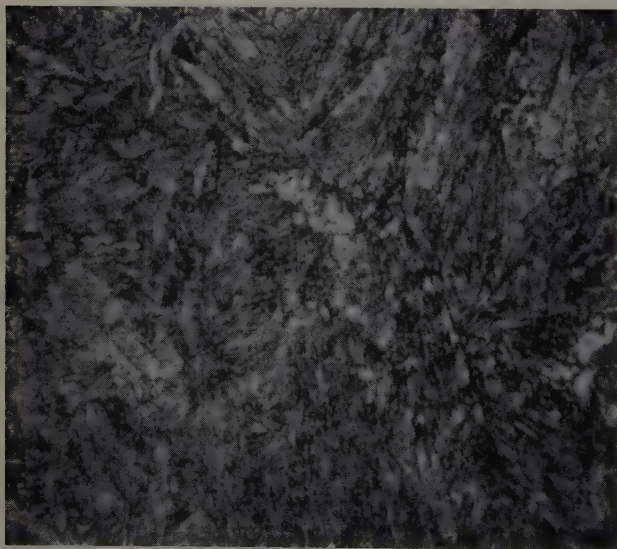


Fig. 25—Tempered martensite 0.87 pct C steel made with an interference filter transmitting  $\lambda 4200\text{\AA}$ .





Fig. 26—Ultraviolet microscopy. Pearlite, 1300°F, 0.87 pct C steel. a (left)— $\lambda 5460\text{\AA}$ . b (right)— $\lambda 3650\text{\AA}$ . X2000.

is of unquestionable value. However, in many applications of ferrous metallography, where color differences other than variations in shades of gray are rare, its extended use can hardly be justified. If someday, paralleling the technique of the biologist, we learn to identify constituents or structures in steel by differential staining, then color metallography may become an indispensable tool of steel metallography.

#### Photographic Materials

The metallographer has always been fortunate in having at his command a wealth of photographic emulsions from which to choose one well suited to the contrast of his subject. Yet, from the beginning the tendency has been to use exclusively glass plates coated with emulsions of high contrast. For a high percentage of micrographs emulsions of high contrast are the correct choice, although their exclusive use often results in unpleasant black and white reproductions devoid of half tones. But regardless of the type employed there is no valid reason why an emulsion intended for metallography should be coated on glass rather than on film. We are told that the superior flatness of plate glass is desirable for micrography at high power, but actually, except in rare instances when it is desirable to make pre-

cise measurements on the photographic negative, the flatness of films inserted in well-made sheaths is perfectly satisfactory at all magnifications.

There are two distinct disadvantages to glass plates; they are liable to breakage and, because of their bulk and weight they require specially strong cabinets for filing and storage and much floor space. One would gladly overlook these disadvantages if in some small measure they were compensated by some advantage in favor of glass plates, but in truth, glass as a supporting medium for emulsions specially compounded for metallography has no merit to justify its continued use. The manufacturers of photographic materials would render a distinct service to metallography if they would coat on film an orthochromatic emulsion of medium speed which could be developed to a wide range of contrast. Such film would not need to be extremely fine grained, since in optical metallography contact printing is the usual practice.

#### Ultraviolet Microscopy

The metallographer has long been interested in ultraviolet microscopy for two reasons; as a means of increasing resolving power and as a possible means of structural differentiation by differential

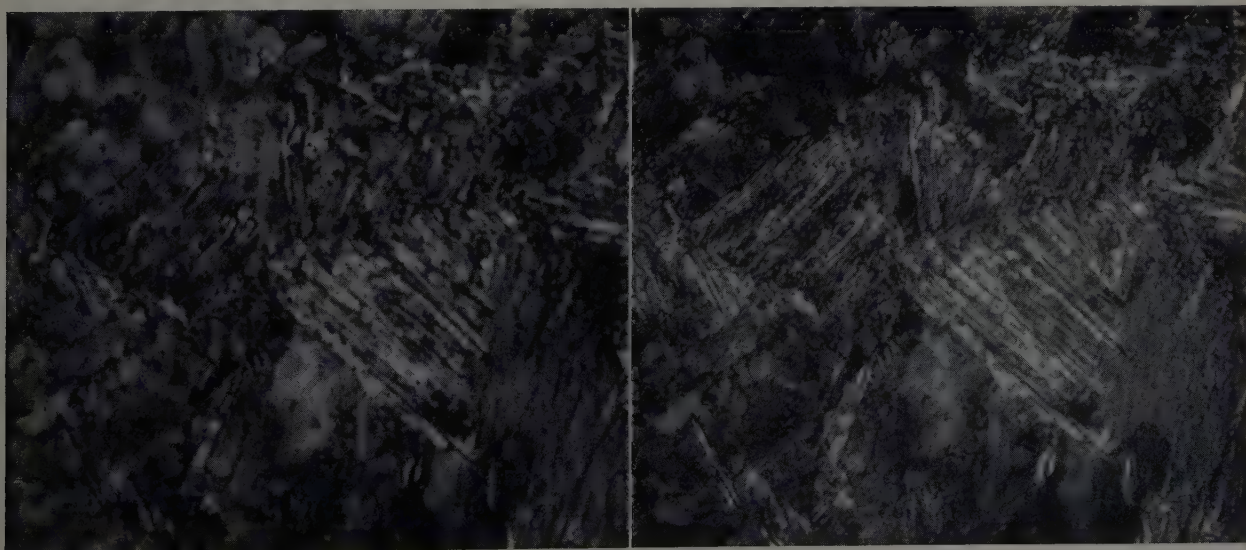


Fig. 27—Ultraviolet microscopy. Fine pearlite and bainite, 950°F, 0.87 pct C steel. a (left)— $\lambda 5460\text{\AA}$ . b (right)— $\lambda 3650\text{\AA}$ . X2000.



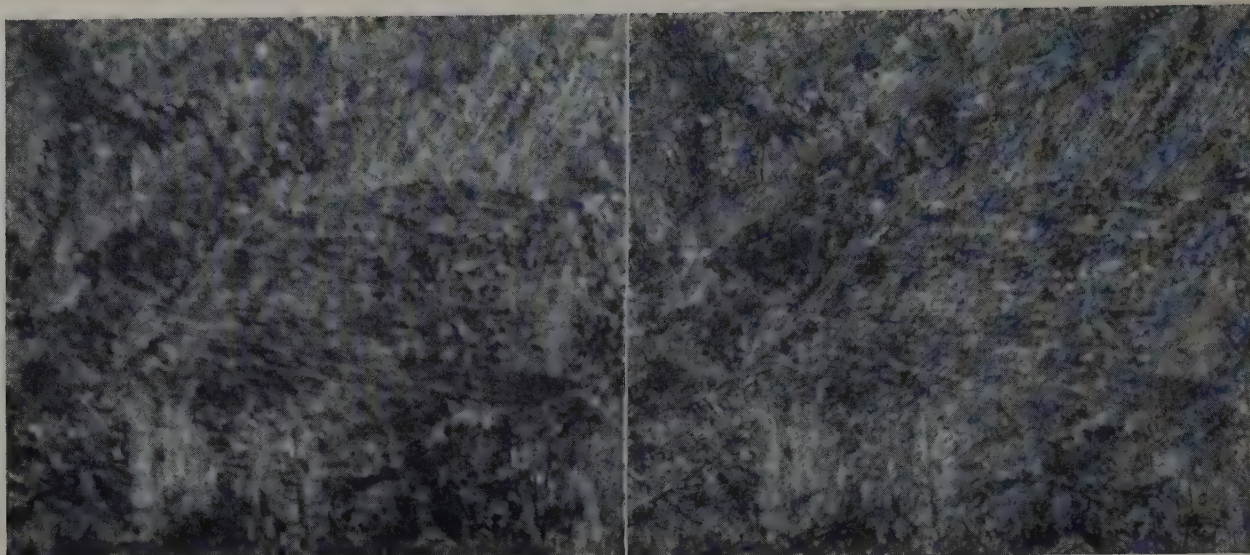


Fig. 28—Ultraviolet microscopy. Bainite, 750°F, 0.87 pct C steel. a (left)— $\lambda 5460\text{\AA}$ . b (right)— $\lambda 3650\text{\AA}$ . X2000.

absorption. The first of these reasons is a reality, the second, a possibility not yet sufficiently explored.

According to Abbe's well-known formula, the resolving power of an objective is proportional to twice the numerical aperture (N.A.) and inversely proportional to the wavelength of the light used. This means that resolution can be improved either by increasing the numerical aperture of the objective or by decreasing the wavelength of the light used. The question of greatest interest to the metallographer is, which of these alternatives is preferable? In answering this question let us consider the extreme differences in numerical aperture existing between electron and light microscopes. The numerical aperture of the magnetic lens of an electron microscope is of the order of 0.001, that is, about 1600 times smaller than that of a 1.6 N.A. monobromonaphthalene immersion objective, which has the greatest aperture of all the objectives available for metallography. On the other hand, the wavelength of the green light generally used in metallography is about  $5500\text{\AA}$  as compared with  $0.05\text{\AA}$  for the electron radiation, that is, the electron microscope employs wavelengths more than 100,000 times finer than those used in the light instrument.

In consequence of these great differences, micrographs made with the extremely small aperture of a magnetic lens are critically sharp and possess remarkable depth and flatness of field even at the highest magnification of the electron instrument, while those made with a light microscope, because of the relatively wider aperture of glass objectives, are of shallow depth of field and except at low magnification, seldom in optimum focus outside of a small area in the center of the field. Sharp focusing with an electron microscope at any magnification within its range is no problem at all, but making a micrograph in good focus with a 1.6 N.A. objective using blue light at a magnification of 2500 diameters is an achievement, and in all candor, more a matter of good luck than of skill.

The preceding comparison indicates the advantages of increasing resolution by employing illuminants of short wavelength rather than by resorting to objectives of higher numerical aperture. This question was raised because the need for choosing between objectives of high numerical aperture using visible light and objectives of lower aperture using ultraviolet is a distinct possibility in the not too distant future. Even today the metallographer who

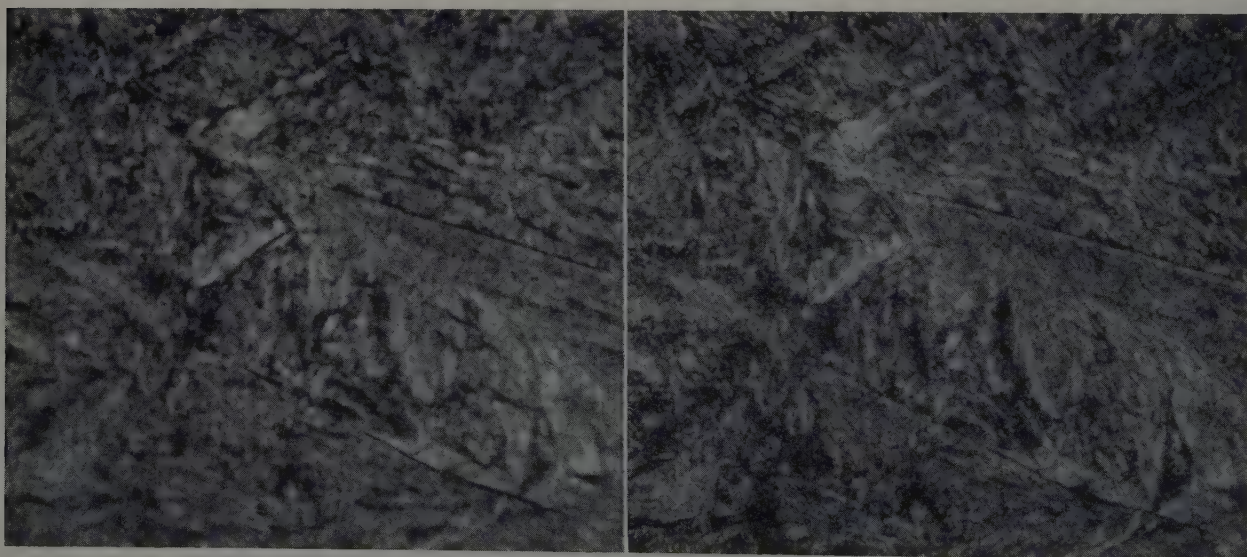


Fig. 29—Ultraviolet microscopy. Tempered martensite, 1 hr at 800°F, 0.87 pct C steel. a (left)— $\lambda 5460\text{\AA}$ . b (right)— $\lambda 3650\text{\AA}$ . X2000.



wishes to resolve the finest detail possible with an ordinary metallurgical microscope has a choice of two objectives of approximately equal resolving power, one of numerical aperture 1.6 corrected for blue light of wavelength in the vicinity of 4500Å and one of numerical aperture 1.3 corrected for ultraviolet light of 3650Å. The theoretical limit of resolving power of both objectives is about 0.14 microns.

The ultraviolet objective referred to is not a recent development;<sup>30</sup> it was manufactured commercially by Bausch and Lomb Optical Co. about 1930, but for some unknown reason it was never used extensively in metallography. It was designed so that the green mercury line with wavelength 5460Å and the ultraviolet of 3650Å are simultaneously in focus. This makes it possible to focus with a green filter, substitute a filter with maximum transmission at 3650Å and make the exposure. Since the absorption of ultraviolet light of 3650Å wavelength by glass is slight, no change from glass to quartz of any part of the optical system is necessary. However, oil of sandalwood is preferable to cedar oil for the immersion medium because it absorbs less of this wavelength.

The process is simple and the results are gratifying, as may be judged from Figs. 26 to 29 inclusive. I am unable to present to you a direct comparison of the same structures photographed with a 1.6 N.A. objective using visible light and with the 1.3 N.A. ultraviolet light of 3650Å wavelength, but there is no doubt in my mind that the image of the ultraviolet objective is superior in resolution, flatness, depth of field and in freedom from flare.

A convenient source of ultraviolet light is the high intensity mercury lamp, type H4, obtainable from General Electric Co. or in a housing for micrography from Bausch and Lomb Optical Co. The exposure for micrographs at 2000 diameters using Corning filter No. 5680, 5 mm thick, varies between 5 and 15 min, depending on the speed of the photographic emulsion and the reflectivity of the structure. Since ultraviolet images tend to be low in contrast, high contrast emulsions such as Kodak Process Ortho, or the equivalent product of other manufacturers, are preferable. The resulting negatives possess sufficient contrast to print well on No. 1 contact printing paper.

Another possibility of a practical system of ultraviolet metallography exists in the application in this field of the reflecting objectives recently introduced for ultraviolet microscopy by transmitted light. These lenses have the very attractive property of being achromatic over a wide range of wavelengths, including both visible and ultraviolet portions of the spectrum. They offer the possibility of attaining a resolving power equivalent to that of a refracting objective of numerical aperture 2.0 without the very serious limitations that such an objective would have if it existed. Since they are achromatic for visible and invisible light, focusing for micrography with the shortest wavelengths in the ultraviolet would be no problem. Fig. 30 was made with a water immersion reflecting objective of numerical aperture 1.1, adapted experimentally for use by reflected incident light and loaned to your speaker by Bausch and Lomb Optical Co. This is possibly one of the first micrographs of a metallic specimen made with a reflecting objective.

Since with these objectives it would be possible to photograph a structure with ultraviolet light of

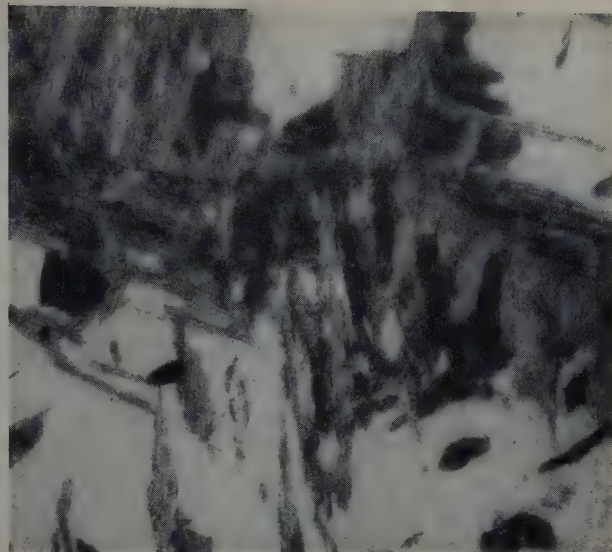


Fig. 30—Ultraviolet microscopy. Bainite. Micrograph made with a reflecting objective using ultraviolet light of  $\lambda 3650\text{\AA}$ . X2000.

different wavelengths, they offer a means of investigating the possibility of identification of structures and constituents by selective absorption.

However, these objectives are not yet available for use in metallography and therefore an appraisal of their contribution to the advancement of our science may have to wait until a future Howe lecturer reviews the achievement of the next twenty-five years.

### Summary

It may be said by way of recapitulation, that the progress achieved in the preceding quarter century in our understanding of the structures of steel was brought about by the following accomplishments:

1—Elimination of disturbed metal from the surface of metallographic specimens. This enabled us to see the true configuration of the structures of steel.

2—Development of the isothermal transformation diagram. This helped us to understand the structures unveiled by the elimination of disturbed metal.

3—Application of the electron microscope to the study of the structures of steel. This enabled us to see finer details than we have seen before and brought us closer to definitive resolution of the structures.

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# Arc Melting of Titanium Metal

by S. F. Radtke, R. M. Scriver, and J. A. Snyder

**An automatic, continuous casting arc furnace employing a nonconsumable electrode and a direct current arc has been constructed and operated successfully for titanium. A comparison of the properties of arc and induction-melted titanium indicates that where high ductility, formability, and toughness are required, arc-melted metal is preferable.**

**B**ECAUSE of the reactivity of titanium metal with all known refractories and the common atmospheric gases, melting of the metal presents numerous problems. It is necessary to provide an inert atmosphere in the furnace as well as a crucible material that will not react with the molten metal, if a ductile ingot is to be produced. Two special furnaces have been developed that meet the requirements and one, the induction heated graphite furnace, has been described in some detail.<sup>1</sup> Little information is available for sizable units wherein power is applied to the melt through an arc, and the dearth of technical information on such a furnace prompted this report. It has been demonstrated clearly that arc melting produces titanium metal with superior toughness, ductility, and formability. To produce titanium ingots with these properties, an automatic, continuous casting arc furnace has been developed and is described herein.

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The history of arc melting may be traced to 1800, when Sir Humphrey Davy<sup>2</sup> first experimented with Volta's electric battery and found that light could be produced and an arc formed between two carbon points attached to the cell. The discovery of the arc was followed by the design and construction of an arc furnace by Napier,<sup>3</sup> in 1845, for the reduction of metal oxides. In 1853, Pichou<sup>4</sup> described a similar furnace, although it was not until the discovery of the dynamo in 1867 that the arc furnace could achieve commercial significance. In 1878, Siemens<sup>5</sup> designed the first arc furnace intended for the melting of metals and by 1882 had melted steel and platinum successfully.

This was followed by Moissan's<sup>6</sup> classical work with the arc furnace in 1892. W. von Bolton,<sup>7</sup> in 1905, found that the arc furnace was suited admirably for melting refractory metals. In his work with tantalum, no suitable refractories for retaining the molten metal were found to exist. Together with Otto Simpson, he developed an arc furnace with a water-cooled copper crucible in which tantalum could be melted without contamination. This technique proved eminently successful.

In his paper on the preparation of ductile titanium, Kroll<sup>8</sup> first described an application of the von Bolton furnace to the melting of this metal. The



The basic principles developed by von Bolton have been applied with increasing frequency in recent years for melting refractory and highly reactive metals on a laboratory and commercial scale. Parke and Ham<sup>9</sup> described a very interesting furnace for arc melting molybdenum, and Eastwood, Simmons, et al.<sup>10</sup> employed the arc furnace in their preparation and study of titanium alloys.

In the development of an arc furnace for melting titanium, a manually operated pilot model was constructed first. From this unit, techniques for feeding titanium sponge, characteristics of inert atmospheres, and the consumption rates of various types of electrode materials were determined. It was found that crushed titanium sponge could be fed at a controllable rate to the furnace chamber by means of a vibratory feeder either continuously or at desired intervals. An atmosphere of argon or helium proved to be satisfactory for manual as well as automatic melting procedures.

During initial runs of the manually operated furnace, it was found that the ingot could be removed continuously at the same rate as sponge was melted in the furnace. Operating at a slight positive internal pressure, it was possible to maintain an effective seal between the ingot and the crucible wall. If a leak occurred, the inert atmosphere bleeding outward prevented the ingress of air.

With the above data available, the furnace illustrated in Fig. 1 was designed and constructed. The furnace proper is entirely water-jacketed, including the crucible, furnace neck, furnace head, and electrode assembly. An auxiliary pump circulates water through the system, the major portion of which is recycled. The ingot, 5¾ in. in diam, may be cast continuously by retracting it at a uniform rate by means of a hydraulic ram. Because of the desirability of having a rugged crucible that could stand constant use without frequent replacement, thin-walled copper crucible sleeves were replaced with extra heavy sleeves of copper pipe. This latter type of crucible has proved very satisfactory.

FIG. 1

FEED HOPPER

FEED TROUGH

BOORMOOD BALL VALVE

SYNCHRON FEEDER

ROTATION MOTOR

WATER INLET

WATER OUTLET

ELECTRODE CABLES

TRAVEL MOTOR

AUTOMATIC ELECTRODE ASSEMBLY

SIGHT GLASS

WATER COOLED HEAD PLATE

WATER COOLED CONDUIBLE NECK

WATER COOLED CONDUIBLE

WATER COOLED ELECTRODE

INSHOT

INSHOT ADAPTER

INSHOT RETRACTOR

top of the furnace through the head to the ingot surface. This shaft, rotated by a motor mounted on the electrode support, revolves an offset electrode holder and permits the electrode to cover the surface of the molten pool. Any variation in the potential across the arc actuates the racking motor which automatically raises or lowers the electrode to regain the desired operating voltage. By such a technique, constant power input to the melt is maintained.

## Operation and Scope

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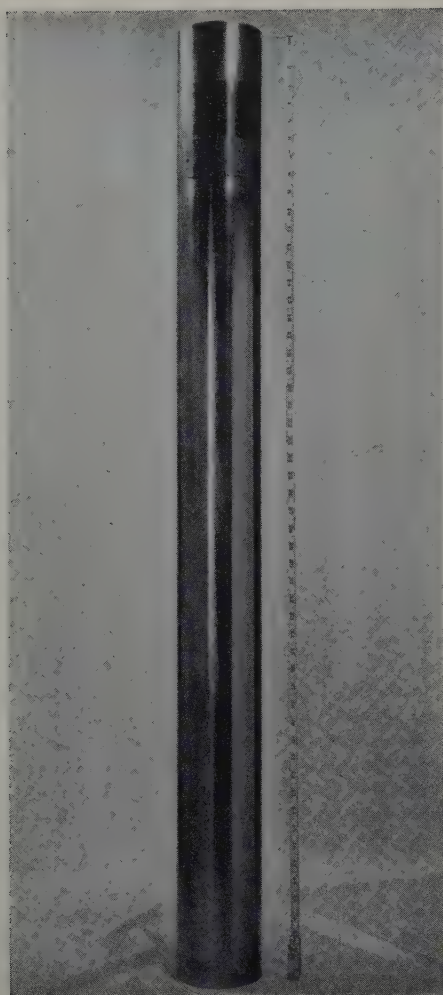


Fig. 2—Titanium ingots up to about 60 in. are continuously cast from the furnace.

thrown in. The electrode, based upon a pre-set voltage, is lowered automatically to strike an arc. After the arc is struck, the electrode rises until the desired potential is attained. The electrode, driven by the rotor motor, begins to rotate and move the arc over the ingot surface.

When the surface of the stub ingot becomes molten, the feeder switch is turned on and in each rotation of the electrode, sponge is fed into the crucible.

As soon as the feed is started, the ingot retractor is set in motion, and the speed of ingot withdrawal is adjusted to conform to the rate of sponge feed. After these manipulations are carried out by the furnace operator, no further work is required of him, except to check the furnace controls. Should the arc be broken for any reason, the control mechanism automatically restrikes the arc. Thus after the furnace is started, the melt is carried out completely automatically.

Commercially pure sponge can be melted at a rate of 0.6 to 1.0 lb per min with a power input of 64 to 100 kw. Alloys can be melted at an even higher rate, provided that they have a lower melting point than pure titanium.

The furnace operation is believed safe. Should the crucible be burned through for any reason, the pressure developed by the steam generated would break either the large rupture disk in the feed hopper or in the furnace head. At the same time, the vapor formed would extinguish the arc and open the electrical circuit.

Two furnaces of this type are now in operation. They have demonstrated the feasibility of this basic design and are paving the way for large-scale automatic, continuous casting furnaces. In addition to casting titanium, this type of furnace could be employed for other metals whose reactivity requires the use of an inert atmosphere and a chemically inert crucible.

Alloys of titanium as well as pure titanium can be melted in this furnace. Sponge of relatively uniform particle size usually is tumbled with the powdered alloying elements in an inert atmosphere. After blending, the alloying powders fill the interstices of the sponge and leave little if any residual powder in the blender. If metal powders are not used, the alloying metals should be screened to a relatively uniform size before blending with the sponge. This method has been used successfully for a variety of alloys. A continuously cast ingot 4 ft 5 in. in length and scalped to a depth of  $\frac{1}{4}$  in. on the diameter is shown in Fig. 2.

Although this discussion has been limited primarily to an arc furnace of the nonconsumable electrode type, it has been shown to be feasible to melt titanium as a consumable electrode. The basic furnace described herein need be modified only slightly to accomplish this end.

### Characteristics of Ingots

If arc-melted ingots are allowed to cool to room temperature before being removed from the furnace,



Fig. 3—This shows the top of a typical ingot produced by arc melting. It is in the as-cast condition, enlarged 2X. This ingot is actually  $5\frac{3}{4}$  in. diam, but a reduction in size was necessary to reproduce the photograph.



the top of the ingot appears as a bright, shiny surface with the grain boundaries clearly delineated. The top of a typical ingot is shown in Fig. 3. When a hot ingot is removed from the furnace, a thin oxide film is formed on the entire ingot surface. The oxide film formed on continuously cast ingots is very thin and is not considered objectionable. For this reason, and the fact that all subsequent hot-working of the ingot is done in air, no effort has been made to prevent oxide film formation during the continuous casting operation. The side of the ingot presents a slightly rippled surface, Fig. 4. This ingot was furnace-cooled and presents a bright metallic surface. To produce a void-free surface, it usually is necessary to remove from  $\frac{1}{8}$  to  $\frac{1}{4}$  in. on the diameter. Any minor voids which then appear at the surface can be removed readily by surface grinding. After the above operations, the ingot is ready for forging.

Although Fig. 3 indicates that the grains might possibly be equiaxed and of relatively uniform size, such is not the case. Several ingots have been cross-sectioned to determine the longitudinal grain configuration. These ingots, as typified by the ingot shown in Fig. 5, have long grains growing from the bottom of the ingot toward the top. Grains up to 10 in. long have been noted. Small, preferentially oriented grains are found at the mold surfaces. In general, the structure of arc-melted material is typical of that obtained in chill-case ingots. The ingots as-cast are usually sound and free from extensive porosity. It has been found that internal pores which may occur in arc-melted ingots seal up readily when the ingot is forged, while external defects usually result in cracking.



Fig. 4—The surface of an as-cast ingot is relatively in good condition, as shown in this  $1\frac{1}{2}$  diam enlargement.



Fig. 5—An as-cast arc-melted ingot etched with HF-HNO<sub>3</sub> shows columnar grain structure. X3.

Despite the fact that the feed metal is contaminated to the extent of about 0.2 pct by the graphite electrode employed during melting, this is virtually the only contaminant added to the melt. In batch melting, a static sealed inert atmosphere is employed which, if gettered by passing over hot titanium sponge, will reduce the contamination by oxygen and nitrogen to trace amounts. In continuous casting, nitrogen contamination can be held at virtually the same level if gettered gas is employed, since the rate of flow of helium required to maintain a slight positive pressure in the furnace is only of the order of 0.5 cfm. With the exception of an arc furnace em-



Fig. 6—This section of arc-melted titanium sheet, etched with HF-HNO<sub>3</sub> and enlarged 250X, shows grain structure of rolled material.



Table I—Typical Physical Properties of Arc Melted, Induction Melted, and Iodide Titanium

|                                          | 0.2 Pct Offset<br>Yield<br>Strength,<br>psi | Ultimate<br>Strength,<br>psi | Elongation<br>in 2 In.,<br>Pct | Reduction<br>of Area,<br>Pct | Minimum<br>Bend<br>Radius<br>75°<br>(Times<br>Thickness<br>of Metal) | Vickers<br>Hardness<br>Number |
|------------------------------------------|---------------------------------------------|------------------------------|--------------------------------|------------------------------|----------------------------------------------------------------------|-------------------------------|
| Arc-melted titanium                      |                                             |                              |                                |                              |                                                                      |                               |
| Forged bar <sup>12</sup>                 | 80,000-85,000                               | 90,000-95,000                | 15-25                          | 30                           |                                                                      | 200-250                       |
| Regular annealed sheet <sup>13</sup>     | 70,000-80,000                               | 80,000-90,000                | 15-20                          | 55                           | 2-2.5                                                                | 200-250                       |
| High purity annealed sheet <sup>13</sup> | 55,000                                      | 65,000                       | 25                             | 60                           | 1.5-2.0                                                              | 170-200                       |
| Induction-melted titanium                |                                             |                              |                                |                              |                                                                      |                               |
| Forged bar <sup>12</sup>                 | 80,000-85,000                               | 90,000-100,000               | 10-15                          | 20                           |                                                                      | 225-275                       |
| Annealed sheet <sup>12</sup>             | 80,000-85,000                               | 90,000-95,000                | 10-20                          | 10                           | 3-4                                                                  | 225-275                       |
| Arc-melted iodide titanium               |                                             |                              |                                |                              |                                                                      |                               |
| Annealed sheet <sup>14</sup>             | 22,000                                      | 46,000                       | 50                             | 60                           | 0                                                                    | 90-110                        |
| Charpy V-notch impact strengths          |                                             |                              |                                |                              |                                                                      |                               |
| Testing temperature                      |                                             | Room temperature             |                                | 500°F                        |                                                                      |                               |
| Arc-melted titanium <sup>12</sup>        |                                             | 18 ft-lb.                    |                                | 60 ft-lb.                    |                                                                      |                               |
| Induction-melted titanium <sup>12</sup>  |                                             | 9 ft-lb.                     |                                | 35 ft-lb.                    |                                                                      |                               |

playing a consumable titanium electrode, the non-consumable electrode technique produces titanium ingots of the highest purity.

### Properties of Arc-Melted Titanium

The physical properties of arc-melted titanium of commercial purity are intermediate between those of high purity titanium made by the iodide process and induction-melted metal. Arc-melted titanium shows much higher strength than iodide titanium and can be rolled readily to thin sheets that can be fabricated by standard techniques. While induction-melted titanium containing 0.4 pct C and above has slightly higher strength, sheet rolled from this material shows lower formability and requires larger bend radii. In addition, the toughness of induction-melted material, as indicated by Charpy V-notch impact tests, is only half that of arc-melted titanium. A tabulation of typical physical properties of arc-melted, induction-melted, and iodide titanium is presented in Table I. The microstructure of sheet rolled from arc-melted titanium is typified by that shown in Fig. 6.

The microstructure of annealed, arc-melted titanium sheet shows a matrix of irregularly shaped grains of  $\alpha$  titanium. Carbides usually are present in relief because of their high hardness. There are also a number of small dark etching particles which seem quite numerous for a metal with less than 1 pct of impurities. The exact nature of these dark etching particles has not been determined.

Arc-melted titanium is preferred for the production of sheet metal as the higher purity results in material with greater ductility and formability. Annealed sheet with an 0.2 pct offset yield strength of 80,000 psi can be bent around a mandrel with a radius that is only double the sheet thickness. The ductility of titanium is restricted by its hexagonal structure, and at room temperature titanium deforms by slip along the basal planes of the crystals. The additional work performed during rolling, as compared to a bar that is only forged, seems to improve the ductility of the finished sheet.

Impact tests of arc-melted titanium show breaking strengths almost double those for induction-melted metal. Values listed in Table I were for small ingots forged to ½ in. square bars.

From the data presented in Table I, it may be seen clearly that arc-melted titanium has higher form-

ability and toughness than induction-melted metal containing carbon above 0.4 pct. For end uses where these properties are required, it will be necessary to melt sponge titanium by arc melting or similar techniques, hence, the need for developing arc-melting know-how.

### Summary

An automatic, continuous casting arc furnace employing a direct current arc has been constructed and operated successfully. While designed specifically for melting and casting titanium it can be employed for melting other reactive metals. Comparative properties of arc and induction-melted titanium indicate that where high ductility and formability and toughness are required, arc-melted material is preferable.

### Acknowledgment

The electrode mechanism and electrode control circuit of the arc furnace described herein were designed in conjunction with Mark F. Gouran, Philadelphia.

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# Powder Metallurgy of Zirconium

by Henry H. Hausner, Herbert S. Kalish, and Roswell P. Angier

**P**OWDER metallurgical methods as applied to zirconium are of great interest because they permit not only the fabrication of parts directly to shape with a minimum loss of material but also the utilization of scrap, and the metal may be processed at temperatures well below the melting point. There are two difficulties involved in the melting of zirconium: 1—High vacuum is necessary for melting, and 2—zirconium reduces nearly all oxides so that it is difficult to find a suitable crucible material. The purest material, zirconium crystal bar, is expensive, and the methods of subsequent fabrication are limited. Cold rolling or extrusion of zirconium crystal bar is suitable for making certain shaped parts, but where melting is involved, the purity of the metal is invariably decreased, and a method of casting to a definite shape does not seem to be feasible.

Where it is necessary to hot roll, zirconium must be covered with a steel or copper jacket to protect it from the air. This is necessarily a costly operation. Where annealing of zirconium is necessary it must be conducted in a high vacuum.

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In an investigation of powder metallurgical methods for zirconium, the zirconium powder used should be characterized by the following properties: 1—Highest degree of purity, 2—uniformity in particle shape and particle size distribution, 3—low compression ratio, and 4—satisfactory strength of the compacted powder (green strength). Zirconium powders have been made by two methods: By the reduction of zirconium tetrachloride ( $ZrCl_4$ ) with sodium,<sup>2, 4, 5</sup> and by the reduction of zirconium oxide with calcium and calcium chloride.<sup>6</sup> The first method represents one of the earliest attempts to make pure zirconium metal, and the sintered product from this powder is extremely brittle. The second method of making zirconium powder is far more successful, but the powder made in this way has an extremely low apparent density and, therefore, a high compression ratio which makes it difficult to use it for powder metallurgical purposes. For these reasons the above-mentioned zirconium powders were not used in this investigation. To obtain sintered zirconium compacts of highest purity and good ductility, it was first necessary to produce a suitable powder.

Pure zirconium has been made chiefly by two methods. The iodide method, from which the product is "crystal bar" zirconium, was developed first.<sup>1-3</sup> By this purification process very soft, pure, and ductile zirconium metal can be produced. The second method, developed by the U. S. Bureau of Mines, is the reduction of zirconium chloride with magnesium.<sup>8</sup> The sponge zirconium thus produced is also soft, pure, and ductile.

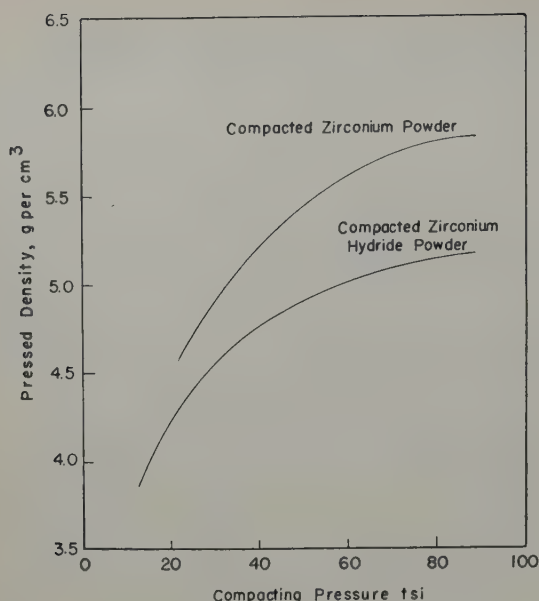


Fig. 1—Effect of compacting pressure on the pressed density of compacted zirconium and zirconium hydride powders.

There are, however, several distinct differences between zirconium produced by these two methods. The sponge metal must be melted and cast to make it suitable for subsequent fabrication, while the crystal bar can be directly rolled or extruded to the desired shape. Both methods yield metal with about 0.5 to 3.0 wt pct hafnium. The melted and cast sponge contains appreciable carbon, about 0.1 wt pct, and perhaps more oxygen and nitrogen than the crystal bar, but it is equally as pure in respect to other elements. Zirconium made from Bureau of Mines sponge is harder, somewhat lower in ductility, and higher in tensile strength than the crystal bar product. These differences may be attributed chiefly to the higher oxygen and carbon content of the zirconium sponge product, although it is not clear what role the carbon plays in affecting physical properties. In order to investigate the powder metallurgy of zirconium, powders made from zirconium crystal bar were used.

### Powder Preparation

**Processing:** Zirconium crystal bar is too ductile at room temperature and even at very low temperatures, such as that of liquid nitrogen, to be comminuted by mechanical methods. Zirconium, however, forms a hydride that is brittle enough to be comminuted mechanically, and the hydride powder then can be readily decomposed in vacuum. Therefore, the hydride method was chosen for the preparation of the powder.

Zirconium hydride forms in the temperature range from about 235° to 800°C.<sup>6</sup> The absorption of hydrogen, whether it goes into solid solution or forms the hydride or both, is most rapid at about 400°C. At this temperature, face-centered tetragonal ZrH<sub>2</sub> forms. Above this temperature ZrH<sub>2</sub> is no longer stable, and hydrogen will be given off, if the sample has been previously heated at 400°C until it has taken up enough hydrogen to form ZrH<sub>2</sub>. At about 800°C the face-centered cubic ZrH forms and can be retained if quenched to room temperature or cooled from this temperature in an inert gas or vacuum. If the ZrH is cooled slowly in hydrogen the formation of ZrH<sub>2</sub> will again occur in the vicinity of

400°C. Above 800°C hydrogen is given off until, at the transformation temperature of 862°C, there is a sudden absorption of hydrogen. Above this temperature hydrogen would again be given off. The mechanism of the formation of ZrH<sub>2</sub>, ZrH, and the solid solution of hydrogen in  $\alpha$  and  $\beta$  Zr is described in the literature.<sup>6-9</sup>

Zirconium hydride was made at 400° and 800°C for subsequent processing. The zirconium hydride made at 400°C was primarily ZrH<sub>2</sub>. At 800°C, ZrH formed, but furnace cooling in hydrogen permitted the formation of ZrH<sub>2</sub> to occur. X-ray analysis revealed that the product of the 800°C treatment was a mixture of ZrH and ZrH<sub>2</sub>, but contained a larger proportion of ZrH<sub>2</sub>. Subsequent to the hydriding process, the friable hydride pieces are ground by hand in a steel mortar with a steel pestle or in a hammer mill to the desired size. Both hydrides are so friable that they can be ground easily to pass a 400 mesh screen (0.037 mm) if that is desired. The product of the 400°C treatment appeared to be more friable, but it took somewhat more grinding to make it fine enough to pass through a 325 mesh screen.

The zirconium metal powder can be prepared by vacuum decomposition of a powdered charge of either of the hydrides, ZrH<sub>2</sub> or ZrH. The decomposition occurs by heating the hydride up to a temperature of 800°C or above in a vacuum of 0.05 micron or better. During the heating operation of the cycle, the pressure of hydrogen in the vacuum system rises to more than 25 microns and then diminishes rapidly to its initial value after being heated for a certain time (depending upon the amount of the charge) at 800°C or above. The slow rate of heating, the fast pumping speed, and the temperature of approximately 800°C are considered critical to the removal of hydrogen to a few hundredths of a percent and the obtaining of a loosely sintered cake of zirconium that can be easily ground to a powder.

The particle size distribution, densities, and apparent densities of the powders obtained by these methods are shown in Table I. Zirconium hydride pulverizes more easily than the zirconium obtained by the decomposition of the hydride and, therefore, contains a larger amount of fine particles. Both powders, zirconium hydride as well as zirconium, contain traces of Al, Ca, Cu, Fe, Mg, Mn, and Si of

Table I. Particle Size Distribution, Density, and Apparent Density of Zirconium Hydride and Zirconium Powder

| Particle Size<br>Microns                  | ZrH <sub>2</sub> Powder,<br>Run No. 33 | Zr Powder<br>Made from ZrH <sub>2</sub> ,<br>Run No. 33 |
|-------------------------------------------|----------------------------------------|---------------------------------------------------------|
| 0-1                                       | 10.2                                   | 1.5                                                     |
| 1-2                                       | 10.3                                   | 2.8                                                     |
| 2-3                                       | 13.3                                   | 2.0                                                     |
| 3-4                                       | 19.0                                   | 4.3                                                     |
| 4-5                                       | 8.3                                    | 3.8                                                     |
| 5-6                                       | 5.0                                    | 5.4                                                     |
| 6-8                                       | 5.4                                    | 6.6                                                     |
| 8-10                                      | 1.8                                    | 5.5                                                     |
| 10-12                                     | 1.1                                    | 5.3                                                     |
| 12-14                                     | 1.3                                    | 5.6                                                     |
| 14-16                                     | 1.5                                    | 5.5                                                     |
| 16-20                                     | 1.8                                    | 8.0                                                     |
| 20-30                                     | 7.7                                    | 15.4                                                    |
| 30-44                                     | 10.5                                   | 19.4                                                    |
| 44                                        | 2.3                                    | 8.9                                                     |
| Photolumetric<br>average size,<br>microns | 10.3                                   | 20.0                                                    |
| Particle density,<br>g per cc             | 5.72                                   | 6.59                                                    |
| Apparent density,<br>g per cc             | 2.2                                    | 2.0                                                     |



practically the same amount as found in the zirconium crystal bar from which the hydride was made. Chemical analysis revealed the presence of gaseous impurities, i. e. 0.2 to 0.4 pct O and 0.01 to 0.015 pct N. There was very little difference in the particle shape of the three kinds of powders, ZrH, ZrH<sub>2</sub>, and Zr. All particles were of angular shape, similar to most particles obtained by crushing.

**Equipment:** The equipment for the preparation of the hydride comprises a quartz tube electric furnace and a hydrogen purification train. Formation of zirconium hydride requires the use of highly purified hydrogen, if the purity of the powder is to be maintained. Tank hydrogen which is reported to contain 0.2 pct O and no other appreciable impurities, was passed over copper turnings at 600°C to catalyze the reaction between hydrogen and oxygen to form water. The water was removed by activated alumina (Lectrodryer). A furnace, containing calcium turnings at 700°C, was used to remove the last traces of oxygen, nitrogen, and water. This purified hydrogen was permitted to flow over the zirconium crystal bar during the entire processing of the zirconium hydride, including the heating and cooling cycles. The charge was maintained at a temperature of 400° or 800°C for 1 to 20 hr, depending on the amount of zirconium, and the furnace was cooled in the hydrogen flow.

The vacuum furnace (globar type) used for the decomposition of the hydride powder to zirconium powder contains a sillimanite furnace tube and comprises a compound model CVD Kinney pump and a Distillation Products MC-500 metal diffusion pump.

### Processing Methods

**Compacting of Zirconium and Zirconium Hydride Powders:** Both zirconium powder and zirconium hydride powder can be compacted without the use of a binder. The powders flow easily and the filling of the compacting die can be done without any difficulties. The powder within the die cavity is levelled as easily as any conventional commercial metal powder.

The compression ratio is defined as the ratio of the volume of a loose powder to the volume of the compact after application of a specified pressure.

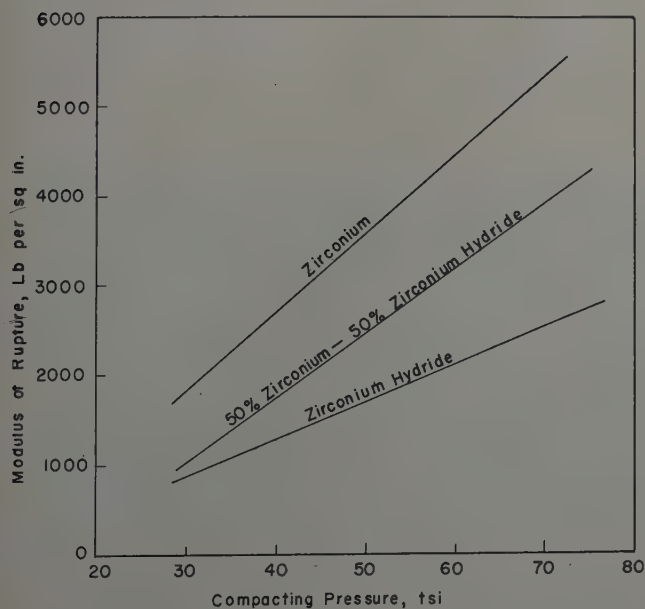


Fig. 2—Green strength of compacted —200 mesh zirconium and zirconium hydride powders.

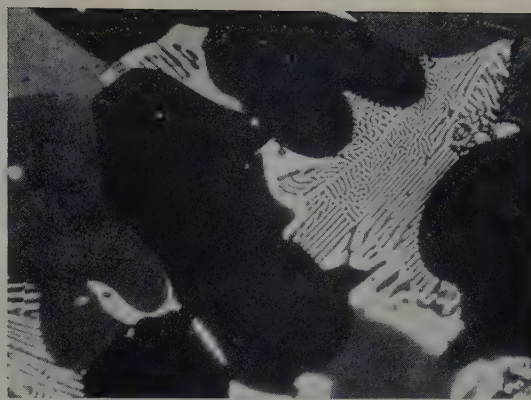


Fig. 3—Effect of BeO on zirconium at sintering temperatures. Microstructure of the interior of a zirconium bar packed in BeO powder and heated 4 hr at 1250°C in high vacuum. Polarized light. X250. Area reduced approximately 50 pct for reproduction.

This ratio is low for both powders, as mentioned above. When conventional pressures of 40 to 50 tons per sq in. (tsi) are applied, the compression ratio ranges between 2:1 to 2.5:1. Inasmuch as the compression ratio determines the height of the compacting die, the low compression ratio of zirconium and zirconium hydride powders is very favorable for the die design.

Fig. 1 shows the effect of the compacting pressure on the density of the compacts made from zirconium hydride and zirconium powder. The powders were pressed in a single-action die of 3/8x2 in. die cavity at pressures varying from 20 to 90 tsi. Higher densities of the compacts may be obtained by using double-action dies or by pressing samples with a more favorable ratio between pressing area and die-wall area. The application of 100 tsi compacting pressure resulted in slightly higher density, but some of the compacts, pressed at 100 tsi, showed indications of lamination.

To determine the relative green strength of this compacted material, zirconium powder, zirconium hydride powder, and a mixture of 50 pct zirconium and 50 pct zirconium hydride powders were pressed at 30 and 70 tsi. Three samples of each type of approximately 1/8x3/8x2 in. were compacted at each pressure in the above described rectangular, single-action die. The compacts were placed on semi-knife edge supports which were 1 in. apart and loaded transversely with a dead load suspended from a semi-knife edge. The load was increased constantly until the sample broke. The differences in modulus of rupture between samples of the same material compacted at the same pressure correlated the slight differences in density that occurred from sample to sample. The data are presented in Fig. 2. There is probably some deviation from a straight line particularly at higher pressures, but for the present correlation it seems adequate to present the data as shown. The green strength of compacted zirconium is approximately twice as high as the green strength of zirconium hydride compacts. The addition of zirconium powder to zirconium hydride powder increases the green strength of compacts made therefrom.

If the pressed compact were the ultimate product, zirconium powder would be clearly a more suitable material than zirconium hydride. It will be shown later, however, that to produce a sintered material of good density, zirconium hydride can be compacted

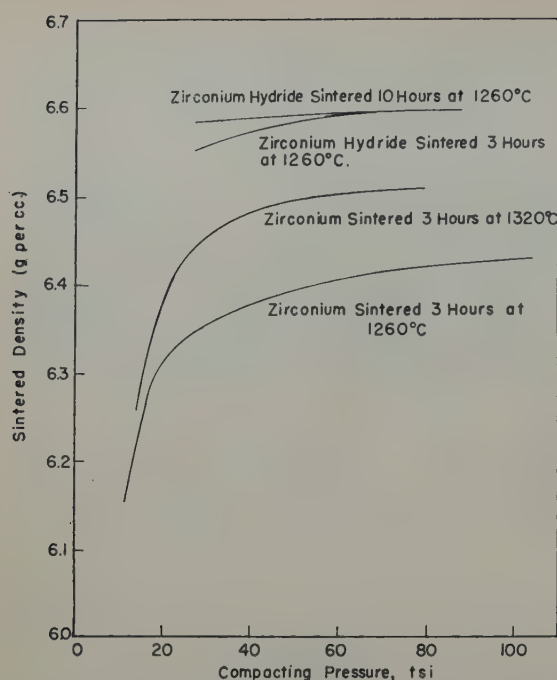


Fig. 4—Effect of compacting pressure on the sintered density of pressed and sintered zirconium and zirconium hydride powders, sintered in high vacua.

at even lower pressures than zirconium powder. In addition, many large thin briquettes, approximately  $\frac{1}{8} \times 2 \times 13$  in., of zirconium hydride have been pressed at pressures as low as 15 tsi without a single loss by breakage.

**Sintering of Zirconium and Zirconium Hydride:** The extreme affinity of zirconium for oxygen and nitrogen<sup>8, 10</sup> makes it necessary to sinter in either a very pure inert gas or in a high vacuum. Compacted zirconium powder was sintered in purified argon. Even though the tank argon was purified by hot copper turnings, a Lectrodryer, drying towers of phosphorous pentoxide and magnesium perchlorate, and hot uranium turnings, it was not pure enough for the sintering of zirconium. The last traces of nitrogen could not be removed completely from the argon by the hot uranium turnings, and the zirconium invariably picked up excessive nitrogen. Sintering in vacuum of the order of  $5 \times 10^{-5}$  mm Hg or better was carried out successfully at temperatures of 1300°C or less without any noticeable in-

crease in oxygen or nitrogen content. Vacuum sintering was also advantageous because compacted zirconium hydride powder could be sintered directly, thereby eliminating a step in the process. When compacted zirconium hydride powder was sintered in purified argon, the residual hydrogen content was always high, but vacuum sintering reduced the hydrogen content to that of the original crystal bar.

When a compact of zirconium hydride powder is heated in vacuum above 400°C, an appreciable decomposition of the hydride occurs that is closely related with a considerable increase of the mobility of the metallic atoms. The degree of mobility of the metallic atoms at the temperature of the decomposition corresponds to far higher temperatures than those at which the decomposition actually takes place. When the hydride is destroyed, the metallic atoms are at a certain state of unstability that leads to their increased mobility. Because of the high degree of mobility, the metal atoms will migrate until they have found positions corresponding to a minimum of free energy. This process causes a faster rate in sintering of the compacts made from zirconium hydride powder compared to the sintering rate of compacts made from metal powder.

In sintering it is frequently desirable to pack the compacts in a refractory powder in order to have samples of all shapes readily supported and separated during sintering. To investigate the possible use of a packing material, pieces of zirconium crystal bar were packed in different refractory oxides and heated to the sintering temperature of 1250°C in vacuum for 2 hr. X-ray analysis revealed that during sintering the zirconium reduced BeO, SiO<sub>2</sub>, and ZrO<sub>2</sub>, and became contaminated with oxygen and Be or Si. Fig. 3 shows the extent to which zirconium reacted with BeO. The interior of the crystal bar after being heated in BeO powder revealed the typical Zr-Be eutectic structure, as described previously,<sup>11</sup> characteristic of about 2 to 5 wt pct Be. Melting was, of course, evident in this sample by the appearance after the 1250°C treatment. The use of a packing medium of refractory was abandoned because it was expected that even if no reaction occurred the out-gassing of the refractory powder surrounding the zirconium would increase the gas content during sintering.

Stabilized zirconium oxide boats and slabs were used with some success for sintering since the contact with the refractory was not so intimate that much reduction of the ZrO<sub>2</sub> could occur. Even so, the

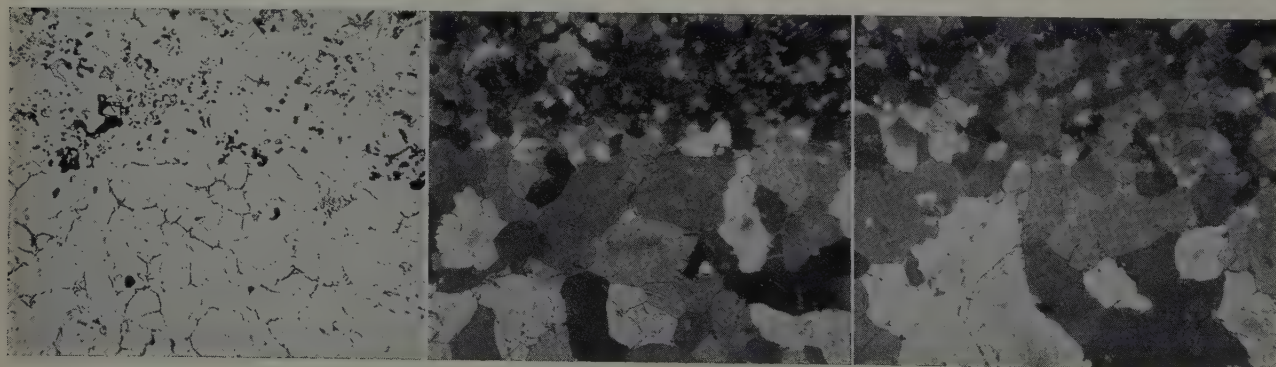


Fig. 5—Interface between zirconium and zirconium hydride. Zirconium hydride powder (shown after sintering on the bottom) placed in the die and pressed at 7 tsi. Zirconium powder (shown on top) added and the entire compact was pressed at 50 tsi. Sintered as indicated in high vacuum. a (left)—Sintered 2 hr at 1190°C. Bright field. b (center)—Sintered 2 hr at 1190°C. Polarized light. c (right)—Same sample as b. Resintered 2 hr at 1300°C. Polarized light. X100. Area reduced approximately 50 pct for reproduction.



reduction of the  $\text{ZrO}_2$  was a possible source of oxygen pickup, and the difficulty in obtaining large boats of stabilized zirconium oxide prompted a search for a better container for sintering.

It was found that samples in intimate contact with graphite did not pick up carbon. Graphite adhered to small areas of the resting surface of the sample, but the carbon penetration was never more than a few mils even after sintering at  $1390^\circ\text{C}$ . Samples sintered in a covered graphite boat and separated by graphite slabs had bright, shiny surfaces. Pieces of zirconium crystal bar revealed no oxygen or nitrogen pickup after being heated in these graphite boats for as long as 10 hr at  $1260^\circ\text{C}$  in a vacuum of about  $2 \times 10^{-5}$  mm. The excellent surface appearance, freedom from contamination, and ease of preparation of graphite boats and slabs of any size made the use of covered graphite boats the most desirable container for sintering zirconium.

In the discussion of the properties of sintered zirconium and other information on the powder metallurgy of zirconium, the powder used for compacting and sintering is zirconium hydride. It is essential, then, that the relative merits of pressed and sintered zirconium powder and zirconium hydride powder be discussed before eliminating the former in the general discussion.

Earlier unpublished work by Angier and Hausner clearly indicated that the sintered product of compacted zirconium hydride powder is superior in most respects to that of zirconium powder, i.e., the ductility, corrosion resistance, and gas content was more favorable in the former. Obviously these superior properties are a function of the lower oxygen and nitrogen content, the source of this added gas being in the extra pulverization step necessary to produce zirconium powder. Fig. 4 shows that compacted zirconium hydride sinters readily to the full density of zirconium and that it is comparatively insensitive to differences in compacting pressure in the range shown. In reality, then, if the full density of zirconium is to be obtained, zirconium hydride powder can be compacted at lower pressures than zirconium powder. The inferior green strength of compacted zirconium hydride powder is a small sacrifice for the other benefits obtained, especially since the green strength of these compacts pressed at practicable pressures is sufficient to make them easy to handle.

A test was made to determine if compacted zirconium powder could be pressed together with compacted zirconium hydride powder to give a good final bond during sintering. Such a process might have an application in making specialized shapes where the large shrinkage differential between the two types of compacted powders during sintering could be utilized. The process is indeed favorable. As shown in Fig. 5 an excellent bond was developed. This investigation proved, however, to be a more decisive indication of the superiority of zirconium hydride powder than could be determined by other tests. In Fig. 5a, b, and c, the sintered product of compacted zirconium powder is shown on the top and that of compacted zirconium hydride powder on the bottom of the micrographs. The zirconium hydride powder was pressed in a die at 7 tsi and zirconium powder was added, levelled, and the two layer compact pressed together at 50 tsi. The sample was then sintered in high vacuum for 2 hr at  $1190^\circ\text{C}$ . It is evident from Fig. 5a that the zirconium hydride powder yielded a much less porous sintered zirconium

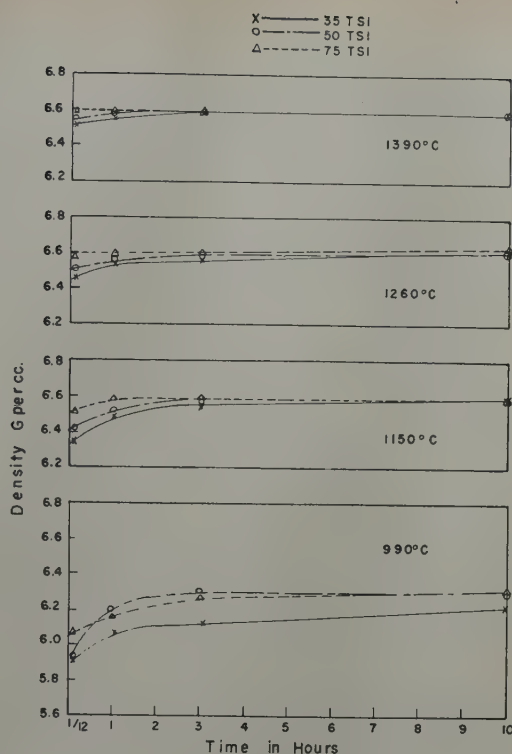


Fig. 6—Effect of sintering time and compacting pressure on the sintered density of zirconium. Samples compacted from zirconium hydride powder and sintered in vacua at various temperatures.

than did the zirconium powder. Fig. 5b shows how the grain growth of the zirconium progressed.

Even though the original particle size of the zirconium hydride powder was much less than that of the zirconium powder, the sintered product of the former has a much coarser grain size. The sintered zirconium powder shows very little if any grain growth at this stage (2 hr at  $1190^\circ\text{C}$ ). However, as would be expected, the sintered zirconium of compacted zirconium hydride shows marked grain growth. In Fig. 5c the resintered sample shows the further progress of grain growth and densification. Evidently the decomposition of zirconium hydride during sintering yields a compact composed of particles that have extremely clean active surfaces ideal for bonding. Whatever the fundamental sintering mechanism may be these highly activated surfaces, then, are ideal for the sintering phenomenon to occur. It is interesting to note that many of the large pores which remain (Fig. 5a and b are identical fields) are within the grains and do not seem to act as barriers to grain growth. This test may be used as another proof that the sintering of compacted zirconium hydride powder may be carried out at lower sintering temperatures and shorter sintering times. There are, then, at least six factors which point to the direct use of zirconium hydride powder for pressing and sintering. These are: 1—Reduction in processing cost of the powder. 2—Reduction in time for processing the powder. 3—Better physical properties of the sintered compact because of lower gas content. 4—Less opportunity for the pickup of impurities during the various processing steps. 5—Permits the use of lower compacting pressure to attain ideal or any arbitrary density. 6—Permits the use of lower sintering temperature and shorter sintering time to attain the ideal or any arbitrary density.

*Hot Pressing of Zirconium Powder:* Tests were

made with pressing of zirconium powder at elevated temperatures. The pressing was done in a graphite-lined steel die at 650°C for 15 min in vacuum at a pressure of 25 tsi. Under these conditions the powder compacted to a solid mass to a density of 6.53 g per cc. The hot-pressed specimens showed uniform fine grain size slightly less than that of cold-pressed and subsequently sintered specimens of similar density. The hardness of the hot-pressed specimen was slightly higher than that of the corresponding cold-compacted and sintered sample.

### Properties of Sintered Zirconium

**Experimental Procedure:** The best processing methods as derived from information incorporated in the preceding sections were utilized to make a comprehensive study of the powder metallurgy of zirconium as processed under a set of standard conditions.

The zirconium hydride was formed at 800°C and ground in a steel mortar and pestle to pass through a 325 mesh screen. One batch of thoroughly blended powder was used for all the tests to be described subsequently thereby eliminating possible variables that may be introduced by variations in the powder.

The samples were compacted in a rectangular steel die 3x1/4 in. to a thickness of about 1/8 in., each sample containing a uniform charge of 7 g of zirconium hydride powder. The compacts were pressed at 35, 50, and 75 tsi, placed in a covered graphite boat, and separated by graphite slabs. The boat was placed in a vacuum furnace, evacuated for at least 16 hr and sintered at 990°, 1150°, 1260°, and 1390°C for 5 min, 1, 3, and 10 hr. During the heating of the specimens the pressure in the furnace tube increased at about 800°C due to decomposition of the zirconium hydride and did not begin to decrease until the temperature was about 950°C. The samples were furnace-cooled in vacuum.

The sintering was done in a global furnace containing a sillimanite tube. This tube was sealed to glass and the entire pumping system up to the mechanical pump was glass. The vacuum was generally about 2x10<sup>-5</sup> mm at temperature. The as-sintered samples had bright, clean, shiny surfaces.

**Densification of the Sintered Compact:** The ultimate

density of compacted and sintered zirconium was investigated as a function of the compacting pressure and sintering variables such as time and temperature. The powder was not varied as pointed out earlier. It is worthy of mention, however, that experiments with zirconium hydride powder ground to a particle size less fine than the —325 mesh did not densify during sintering as readily as the compacted —325 mesh powder at the same time and temperature.

In Fig. 6 the effect of compacting pressure, sintering time, and sintering temperature on the density of zirconium is shown. The role of compacting pressure becomes insignificant at the higher sintering temperatures and longer times. When a minimum of sintering time and the lowest possible temperature is desired, the use of higher pressure becomes important. Ideal density can be attained, for instance, by sintering 1 hr at 1150°C provided a compacting pressure of 75 tsi has been used.

Fig. 7 shows a plot of isodense lines after sintering at any time and temperature in the range shown for compacts pressed at 50 tsi. From this the density obtainable for any given sintering temperature and time can be predicted. The densities would vary, of course, to perhaps ±0.03 g per cu cm because of deviation in both measurement and sample. Compacts pressed at 50 tsi, however, can be sintered to full density as shown by the line for completion of densification. In order to better show the effect of compacting pressure on completion of densification, Fig. 8 is presented. If a sample is to be sintered to ideal density for 8 hr at 1250°C, compacting pressures as low as 35 tsi can be used. If the sintering temperature must be low, however, higher compacting pressures become necessary. At 1100°C, for instance, a sample which has been compacted at 75 tsi can be sintered for as little as 3 hr to attain ideal density.

**Grain Growth:** The grain growth of zirconium during sintering is very rapid provided the material charged to the sintering furnace was compacted zirconium hydride powder. In Fig. 9 the grain size of zirconium, sintered at various times and temperatures, is shown. The actual grain size is shown in microns and in grains per sq mm in Table II.

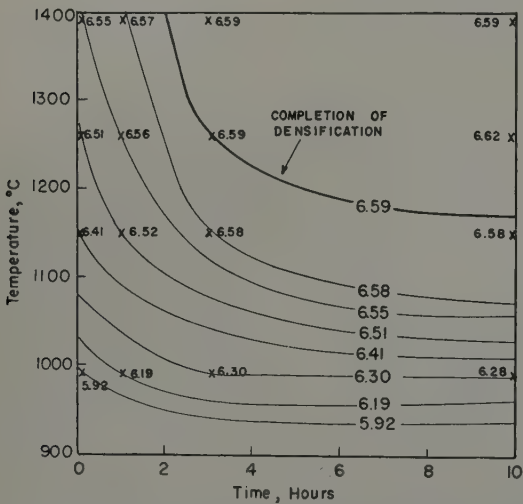


Fig. 7—Constant density lines as a function of sintering time and temperature for zirconium. Vacuum sintered from —325 mesh zirconium hydride powder compacted at 50 tsi.

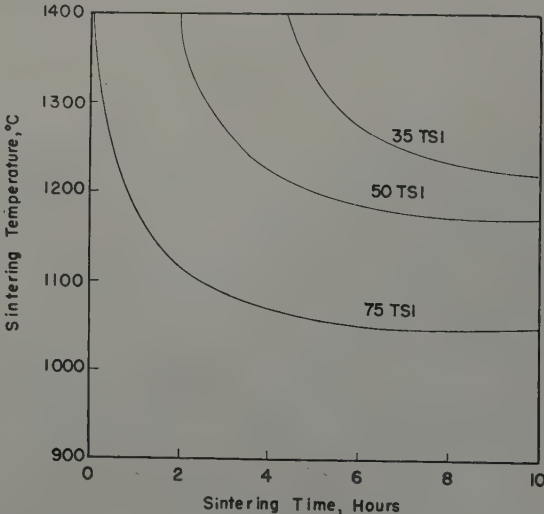


Fig. 8—Isodense lines representing 6.59 g per cu cm (complete densification) for three compacting pressures. Data for —325 mesh zirconium hydride compacted as indicated and vacuum sintered.



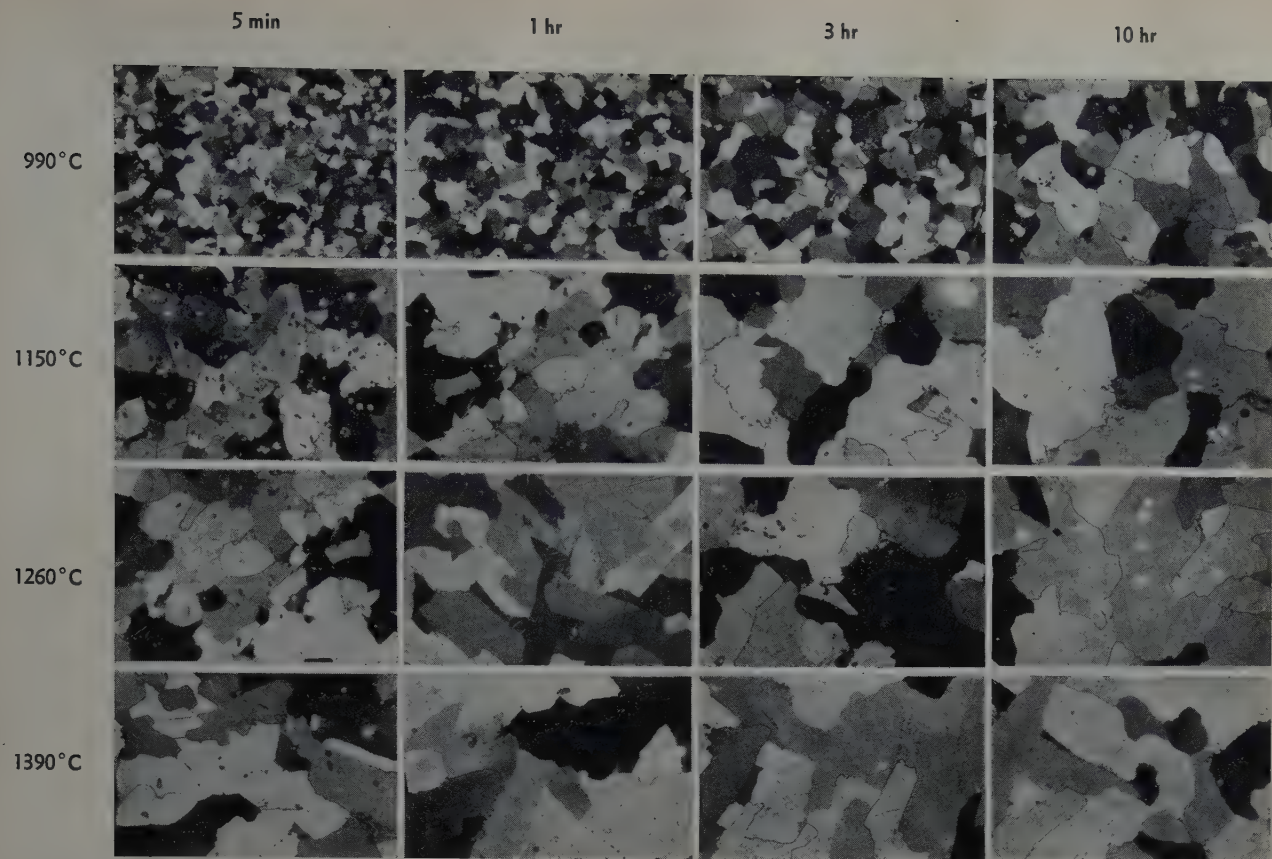


Fig. 9—Effect of sintering time and temperature on the grain growth of zirconium. Compacts pressed at 50 tsi from —325 mesh zirconium hydride powder and sintered in vacuum. X250. Area reduced approximately 80 pct for reproduction.

It appears that grain growth is most rapid in the vicinity of 1100° to 1200°C. At 990°C the growth was quite slow compared to the rapid growth which occurred on sintering at more elevated temperatures. Densification, on the other hand, is relatively rapid at lower temperatures. The relationship between density and grain size is shown in Fig. 10. Initially in the sintering process considerable densification occurs with little grain growth. Toward the end of the sintering process the density becomes asymptotic to ideal and little densification occurs, but grain growth is quite rapid. The relationship between the sintering mechanism and grain boundary movement,

density. After sintering at higher temperatures, the effect of compacting pressure on the hardness becomes negligible. In fact, after a density of about 6.3 g per cu cm is reached, the hardness seems to become insensitive to the slight differences in density.

The hardness of dense sintered zirconium made by these methods is about Rockwell B 92. Variations in hardness may occur so that values from 90 to 94 Rockwell B are obtained. This deviation may be

Table II. Grain Size of Zirconium after Sintering

| Sintering Time | Grain Size, Microns |        |        |        | Grains per Sq Mm |        |        |        |
|----------------|---------------------|--------|--------|--------|------------------|--------|--------|--------|
|                | 990°C               | 1150°C | 1260°C | 1390°C | 990°C            | 1150°C | 1260°C | 1390°C |
| 5 min          | 21.8                | 49.7   | 69.4   | 117    | 2670             | 515    | 265    | 93     |
| 1 hr           | 28.4                | 68.4   | 108    | 131    | 1590             | 208    | 109    | 75     |
| 3 hr           | 31.2                | 107    | 128    | 119    | 1309             | 112    | 79     | 90     |
| 10 hr          | 51.6                | 139    | 143    | 152    | 480              | 66     | 63     | 55     |

if one exists, should have some interesting theoretical ramifications.

**Hardness:** The hardness of sintered zirconium may be influenced among other things by oxygen content, grain size, and density. The first two factors affect the intrinsic properties of the metal, but the hardness when affected by density is merely another indication of the amount of porosity.

In Fig. 11 the hardness is shown as a function of sintering time and compacting pressure for samples sintered at 990°C. It is clear that the only difference in the sintered product affected by compacting pressure is porosity. The differences in hardness, then, shown in Fig. 11, are representative of the trend in

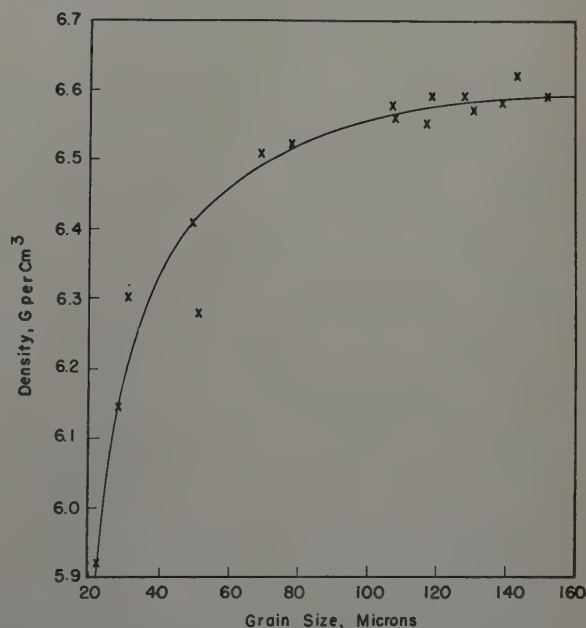


Fig. 10—Relationship between grain size and density of sintered zirconium. Samples compacted at 50 tsi from zirconium hydride powder and sintered in high vacuum at various times and temperatures.

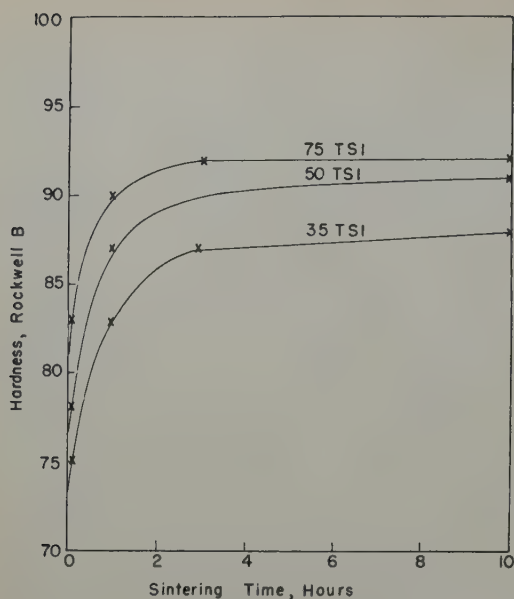


Fig. 11—Effect of compacting pressure and sintering time on the hardness of zirconium sintered in vacuum at 990°C from compacted —325 mesh zirconium hydride powder.

attributed to the variation in grain size and oxygen content, the former influencing lower hardness with more sintering because of grain growth and the latter influencing higher hardness with sintering at higher temperatures or for longer times. It is difficult to isolate the effect of these two variables on the hardness except at 1390°C where the increase in oxygen content noticeably increases the hardness, as shown in Table III. This effect is also clearly illustrated in both the experimental data on electrical resistivity shown in Fig. 12 and the schematic representation, Fig. 13.

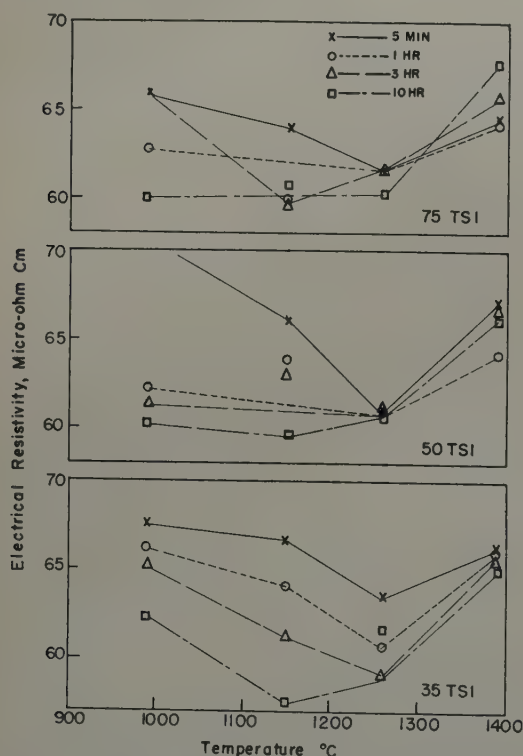


Fig. 12—Electrical resistivity of sintered zirconium compacts pressed as indicated from zirconium hydride powder and sintered in vacuum at the times and temperatures shown.

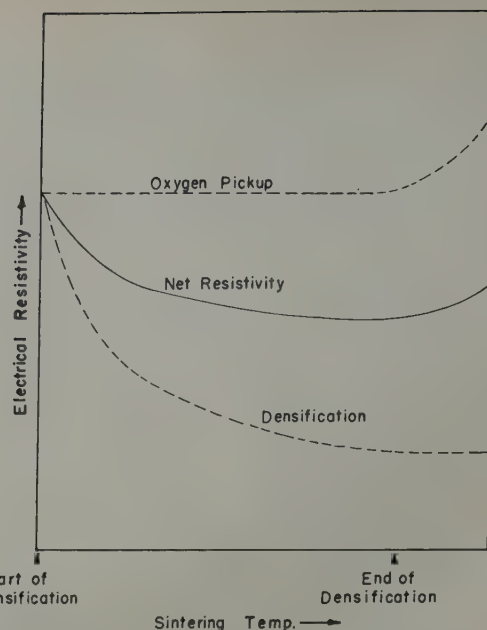


Fig. 13—Idealized curves showing the probable effect of densification and of oxygen pickup during sintering on the electrical resistivity of sintered zirconium.

**Electrical Resistivity:** The electrical resistivity may reflect many variables operating in the processing of sintered zirconium. As explained in the sections on experimental procedure, the control of these experiments was such, however, that many variables can be eliminated from the discussion, and it is indicated that there are only three fundamental differences in the sintered compacts. These are: 1—Grain size, 2—oxygen content, and 3—density. It is probable that grain size would have little if any measurable effect on the resistivity. The two variables which need to be considered, then, are oxygen content and density. The pressed compacts to begin with have an oxygen content of about 0.2 wt pct, the main source of this oxygen being in pulverizing as has been described earlier. Little oxygen is picked up during sintering at temperatures up to 1260°C, but

Table III. Rockwell B Hardness of Sintered Zirconium. Samples Sintered in Vacuum from —325 Mesh Zirconium Hydride Powder Compacted at 50 tsi

| Sintering Time | Sintering Temperature, °C |      |      |      |
|----------------|---------------------------|------|------|------|
|                | 990                       | 1150 | 1260 | 1390 |
| 5 min          | 78                        | 88   | 90   | 95   |
| 1 hr           | 87                        | 93   | 91   | 95   |
| 3 hr           | 92                        | 93   | 92   | 97   |
| 10 hr          | 91                        | 91   | 95   | 98   |

there is some increase at the higher sintering temperatures and very long sintering times. This oxygen which is undoubtedly in solid solution after sintering would have a marked influence on the resistivity.

The electrical resistivity was measured for all sintered samples and these data are shown in Fig. 12. It is immediately apparent that the resistivity first decreases with sintering temperature and then increases. The decrease is definitely due to densification and the increase probably to oxygen pickup. This is shown in the schematic representation in Fig. 13. The resistivity, then, is a splendid guide to optimum sintering conditions, a minimum resistivity



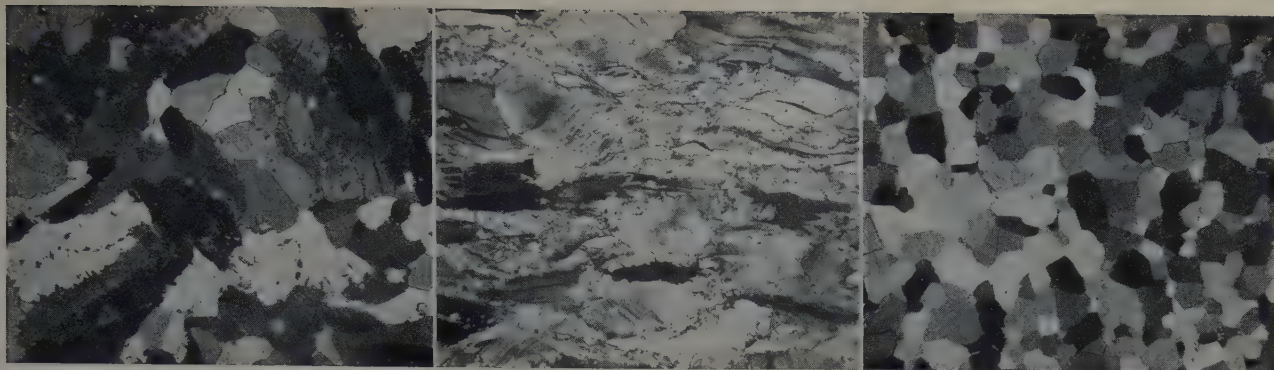


Fig. 14—Microstructure of cold worked and annealed zirconium. Compacted from —325 mesh zirconium hydride powder and sintered 3 hr at 1260°C in high vacuum. a (left)—As sintered. b (center)—Cold rolled 75 pct reduction in thickness, longitudinal section. c (right)—Same as b but annealed 1 hr at 900°C. Polarized light. X200. Area reduced approximately 50 pct for reproduction.

indicating the optimum. From Fig. 12 it appears that the best sintering temperature is in the range 1150° to 1260°C. The data are insufficient to pick a value and establish this as the exact sintering cycle, but a useful sintering range can be ascertained. Compacting pressure plays a role, but the limits on compacting pressure are wide if the selected sintering range is 3 to 10 hr at 1150°C and 1 to 10 hr at 1260°C. This is in agreement with data on the other properties investigated. Samples sintered in these ranges had good density, relatively low hardness, and relatively low oxygen content.

The electrical resistivity of pure zirconium is reported<sup>12-13</sup> to be from 39 to 41 microhm-cm at 0°C, which corresponds to about 40 to 42 microhm-cm at room temperature. The lowest resistivity found in this investigation for sintered zirconium was 58 to 60 microhm-cm at room temperature. The difference between this and the reported electrical resistivity can probably be attributed to the higher oxygen content in the sintered product, which oxygen pickup has occurred during powdering of the zirconium hydride.

**Ductility:** Although tensile tests were not made, cold rolling permitted an evaluation of the ductility of the sintered zirconium. The sintered samples were cold rolled about 5 pct per pass, examined carefully for edge cracking after each pass, and rolling continued until the first sign of edge cracking. Treatment, i.e., compacting pressure, sintering time, and temperature, seemed to have no significant effect on the ductility, practically regardless of the density. In 50 samples of various densities that were cold rolled, the range in reduction of thickness to the first sign of edge cracking was 53 to 72 pct. The average reduction in thickness was 62 pct. The sintered zirconium, then, is quite ductile.

Fig. 14 shows the microstructure of zirconium. These rolling studies proved the existence of a high degree of ductility in sintered zirconium, which makes the powder metallurgy method of manufacturing zirconium parts most valuable.

### Conclusions

Zirconium of high purity can be fabricated by powder metallurgy methods. The use of zirconium hydride powder for compacting and sintering leads to a more superior product than does the use of zirconium powder.

The pressing and sintering conditions that permit the powder metallurgical fabrication of sintered zirconium are established. Compacting at conventional pressure of 40 to 50 tsi, sintering in vacuum within

the temperature range 1150° to 1260°C, and the use of covered graphite boats, during sintering, results in sintered zirconium compacts of practically theoretical density and appreciable ductility.

The superiority of zirconium hydride powder over zirconium powder is shown clearly. It should be useful to determine how well other metal compound powders, such as hydrides, oxides, and others, can be decomposed during sintering and whether this decomposition facilitates the sintering process. Further studies in these directions are under consideration.

### Acknowledgments

We wish to thank H. W. Woods and Eleanor Polukis for their preparation of metallographic specimens, N. P. Pinto for hot pressing studies, H. Mansfield for physical properties testing, and H. B. Michaelson for editorial work. We are particularly indebted to W. E. Kingston for numerous valuable discussions and suggestions regarding this work.

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# Production of Aluminum

from

## Kalunite Alumina

by Arthur Fleischer and Julian Glasser

THIS country was faced with the possible necessity of utilizing nonbauxitic ores for producing aluminum during World War II. Construction of four experimental plants to treat such ores by four different processes was authorized<sup>1-4</sup> including one at Salt Lake City, for the conversion of Marysvale alunite to metal-grade alumina and potassium sulphate by the Kalunite process.<sup>4</sup> An aluminum reduction plant in Tacoma, Wash., with a capacity of 50 tons of aluminum per day, was constructed to handle the Kalunite alumina produced at the Salt Lake City plant. The alumina and aluminum plants were Defense Plant Corp. projects operated by Kalunite, Inc. and Olin Industries, Inc., respectively.

Kalunite alumina differs from Bayer alumina in several respects, particularly in that the former contains potash instead of soda. The presence of potassium in the alumina feed to the cryolite bath was stated by aluminum technologists to be undesirable under the usual operating conditions of

aluminum furnaces. In 1940, about 20 tons of Kalunite alumina produced in the Kalunite pilot plant, were reduced electrolytically in a 10,000 amp furnace at Battelle Memorial Institute and at the aluminum reduction plant at Neuhausen, Switzerland. These relatively small scale tests indicated that satisfactory commercial aluminum could be produced in a practical manner.

The Tacoma plant reduced about 2,500,000 lb of Kalunite alumina to produce more than 1,200,000 lb of aluminum, in accordance with the accepted practice for reducing Bayer alumina. It was desired to determine whether commercial aluminum could be produced on a large scale and to establish the technological differences in commercial reduction practice between Kalunite and Bayer alumina. In the course of collecting data, the effects of the abnormal chemical composition and physical properties of Kalunite alumina were observed wherever possible.

### Tacoma Reduction Plant

The reduction plant had two pot lines, each with 120 cells in series, operated at approximately 32,000 amp. Each cell was provided with a single rectangular Soederberg continuous anode, with side-pin electrical contacts. Each cell was hooded and ventilated through a stack connected to 14 other cells, with 25,000 cfm blower. When the plant started operation in 1942, all of the cathode linings were of block construction. Rebuilt cells were of rammed paste construction.

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A total of 12 cells in pot room No. 1 were operated on Kalunite alumina over a period of 17 months. The remainder of the plant operated on Bayer alumina. Shutdowns immediately after the war brought an abrupt halt to operations.

Operating Conditions

The average charge of alumina was 240 lb to a 9000-lb bath with an average of 3.5 to 3.8 anode effects per day. Normal operating voltage was maintained at 4.9 v and each anode effect (30 to 40 v) averaged 6 min. The crust on alternate sides and both ends of a pot was broken through at anode effects. Before placing a new charge of alumina on the exposed electrolyte, the space between anode and cathode was raked thoroughly. During normal operations, four gas holes, about 6 in. from the anode, were maintained in the crust. Surface temperature of the electrolyte was about 950°C. The ratio of NaF to AlF<sub>3</sub> in the bath was maintained between 1.45 and 1.50. The alumina content in the bath varied between 2 and 7 pct. Anode paste, prepared on the side, was loaded at the rate of about 5000 lb every 15 days. Each pot was tapped every third day, leaving 2 in. of metal pad after each tap.

Since only a small part of the reduction plant was operated on Kalunite alumina, special procedures were required in order to obtain accurate data. Ordinarily, raw material consumption, production, and power data are obtained from overall plant inventories and meter readings from the rectifier station. However, information on a small number of pots cannot be obtained in this manner. Therefore, it was necessary to record weights of all raw materials charged, weight of metal tapped, and voltages for each individual pot operating on Kalunite alumina. To compare the operation with Bayer alumina on the same basis, a section of eight pots was started approximately at the same time and operated for several months, with four each on Bayer and on Kalunite alumina, following identical processing and control procedures.

Each pot was tapped singly with return of all scrap metal to the pot. Total production was obtained from the weight of the as-cast metal. Metal was sampled prior to pouring and analyzed by wet and spectrographic methods. Alumina for each charge was weighed in 60 to 80-lb lots. Each carload of alumina was sampled and analyzed by wet methods. Cryolite and aluminum fluoride were measured from 100-lb sacks. The quantity of anode paste consumed was determined by weights of coke and pitch mixed in the paste plant. Ampere-hours, used for calculating current efficiency and power input, were very accurately measured by the line ampere hour meter. Voltages at each pot were recorded hourly, and voltage and time were recorded for anode effects. A time-weighted average of voltage was used for power input.

Raw Materials

Natural Greenland cryolite, aluminum fluoride, fluorspar, Bayer alumina, calcined petroleum coke for anodes, soft anode pitch, and cathode paste or blocks were purchased on specifications generally

\* The particle size refers here to the aggregates that persist on handling the alumina on the screens. Comparative X-ray diffraction patterns of Kalunite and Bayer aluminas made in 1940 showed that the primary crystallite sizes are the same; diffraction line breadths and intensities agreed very closely. The difference in particle (grain) sizes is to be attributed to the types of aggregation encountered in the two aluminas.

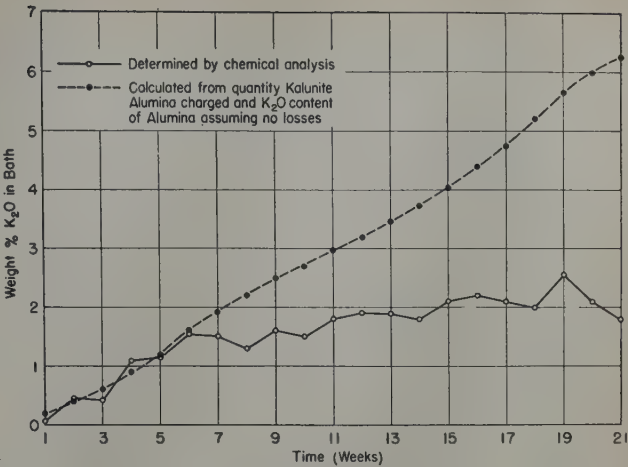


Fig. 1—Potash buildup in electrolyte, pot 95, starting Aug. 13, 1944.

acceptable for aluminum reduction. Typical chemical composition and physical properties of Kalunite and Bayer aluminas are summarized in Table I.

The average chemical composition of the Kalunite alumina showed higher silica, iron oxide, titania, and lead than Bayer alumina. Phosphorous pentoxide, potash and sulphur trioxide were also present in Kalunite alumina in appreciable quantities; but calcium oxide and soda, present in Bayer alumina, were not found in Kalunite alumina. Ignition loss and water absorption were comparable for the two aluminas.

Particle size distribution\* was not nearly so uniform for Kalunite alumina as it was for Bayer alumina. Excessive quantities of both coarse and fine sizing were present.

The uniformity in composition of the Kalunite alumina was poor. For 17 carloads of alumina, sulphur trioxide (SO<sub>3</sub>) varied from 0.40 to 2.30 pct, potash (K<sub>2</sub>O) from 0.25 to 0.78 pct, phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) from 0.01 to 0.08 pct, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) from 0.08 to 0.14 pct, and silica (SiO<sub>2</sub>) from 0.03 to 0.24 pct. This variability in the impurities

Table I. Chemical Composition and Physical Properties of Kalunite and Bayer Aluminas

|                                                       | Kalunite  |                         |                   |
|-------------------------------------------------------|-----------|-------------------------|-------------------|
|                                                       | Typ-ical* | For Compara-tive Data** | Bayer (Typ-ical)* |
| <b>Chemical composition</b>                           |           |                         |                   |
| Silica (SiO <sub>2</sub> )                            | 0.06      | 0.07                    | 0.02              |
| Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )          | 0.12      | 0.12                    | 0.02              |
| Titanium dioxide (TiO <sub>2</sub> )                  | 0.005     | 0.006                   | 0.003             |
| Phosphorus pentoxide (P <sub>2</sub> O <sub>5</sub> ) | 0.06      | 0.09                    | Nil               |
| Potash (K <sub>2</sub> O)                             | 0.35      | 0.38                    | Nil               |
| Sulphur trioxide (SO <sub>3</sub> )                   | 0.91      | 1.24                    | Nil               |
| Soda (Na <sub>2</sub> O)                              | Nil       | Nil                     | 0.45              |
| Calcium oxide (CaO)                                   | Nil       | Nil                     | 0.02              |
| Lead (Pb)                                             | 0.01      | 0.01                    | Nil               |
| <b>Ignition loss and water absorption</b>             |           |                         |                   |
| L.O.I. (1000°C)                                       | 2.09      | 2.37                    | 2.67              |
| Water absorption (bone dry basis)                     | 1.89      | 1.88                    | 3.16              |
| <b>Screen analysis (Tyler mesh)</b>                   |           |                         |                   |
| + 48                                                  | 9.1       | 0.6                     | Nil               |
| - 48 + 100                                            | 14.1      | 5.3                     | 0.5               |
| - 100 + 200                                           | 22.6      | 29.6                    | 53.5              |
| - 200                                                 | 65.4      | 64.5                    | 46.0              |
| - 325 (wet on original sample)                        | 52.0      | n.d.†                   | 12.0              |

\* Average for first half of 1945.  
\*\* Alumina used for data shown in Table II.  
† n.d. not determined, but same order as "Typical."

Table II. Summary of Operational Data, Bayer Alumina vs. Kalunite Alumina

|                            | Kalunite <sup>4</sup> | Bayer <sup>4</sup> |
|----------------------------|-----------------------|--------------------|
| Number of pots             | 4                     | 200                |
| Average age per pot, days  | 173                   |                    |
| Production                 |                       |                    |
| Lb per pot per day         | 405                   | 464                |
| Composition, pct           |                       |                    |
| Al                         | 99.54                 | 99.79              |
| Si                         | 0.18                  | 0.07               |
| Fe                         | 0.25                  | 0.14               |
| Ti                         | 0.01                  | Trace              |
| Pb                         | 0.02                  | Nil                |
| Raw materials consumption, |                       |                    |
| lb per 100 lb production   |                       |                    |
| Alumina                    | 215                   | 189                |
| Cryolite                   | 15.1                  | 9.7                |
| Aluminum fluoride          | 0                     | 1.8                |
| Anode paste                | 72                    | 64                 |
| Skimmings removed          | 2.2                   | 0.6                |
| Current efficiency, pct    | 71.7                  | 82.1               |
| DC kw-hr per lb of metal   | 9.9                   | 8.7                |

was due mainly to unsatisfactory operating conditions and difficulties encountered in the operation of the Salt Lake alumina plant, inflicting the penalties of low capacity operation. The quality of the alumina was lower than that of alumina produced experimentally from alunite ores in laboratory and pilot plant studies.

### Results of Reduction

**Quality of Metal:** Acceptable commercial grades of pig aluminum were produced. In the first half of 1945, 50 pct of the metal produced from Kalunite alumina was 99.60 pct metal (grade B) or better; 4 pct was 2A grade, 99.70 pct metal. To obtain higher grade metal it would be necessary to reduce the impurities in the alumina.

**Operating Record:** The overall operating record for all pots operating on Kalunite alumina showed that commercial alumina could be produced on a large scale without very serious handicaps in production, raw material consumption, and power input. No obnoxious fumes were emitted from the pots, either during normal operation or while breaking in the crust. However, difficulty was experienced in handling the Kalunite alumina, because it was not so free-flowing.

**Effect of Particle Size:** The coarse grain size contained in Kalunite alumina was undoubtedly the most serious factor in disturbing smooth pot operation.\*\* This also masked effects of other abnormal properties of Kalunite alumina. The excessive fine particles caused dust losses. Both the coarse and fine particles were probably responsible for adverse temperature distribution in the pots. The coarse, settling to the cathode bottom, and the fines, acting as a poorer insulator over the crust, would tend to make the bottom hotter. For efficient operation, the cathode should be considerably colder than the anode.

**Potash in Electrolyte:** Of the abnormal impurities in Kalunite alumina, potash appeared to be the only one that was retained in the electrolyte to any appreciable extent. Usually, the potash reached a maximum concentration between 1 and 3 pct in

about six weeks. Apparently a steady state condition was reached whereby the charging and volatilization losses were essentially equal. Fig. 1 illustrates typical data obtained during the operation of one of the cells. The upper limit of potash content of the bath is of the same order of magnitude as previously found in the operation of the 10,000 amp cell at Battelle Memorial Institute during 1940.

**Cathode Lining:** No particular adverse effects were noted on cathode linings. The absorption of potash in the lining was about the same as found for the absorption of soda from Bayer alumina.

**Comparative Reduction Data:** The data have been summarized in Table II. The Kalunite alumina used for comparative reduction data was screened to eliminate most of the excess coarse sizing. As compared to equivalent operation on Bayer alumina, the metal produced contained somewhat higher quantities of silicon, iron, titanium, and lead. Alumina consumed was about 13 pct higher than for Bayer alumina, mostly because of dust losses. No aluminum fluoride was required for the Kalunite alumina operation, because the potash did not continually build up in the bath. The higher rate of carbon dusting from the anodes is reflected in anode paste consumptions and skimmings removed. The current efficiency for pots operating on Kalunite alumina was about 10 pct lower than for those on Bayer alumina.† This caused higher energy input per pound of metal for pots operating on Kalunite alumina. Miscellaneous differences in operating characteristics for pots operating on Kalunite alumina as compared to those on Bayer alumina included lower anode effect voltages, lower bath surface temperatures, less potent anode gas flames, less serious anode corrosion, and less movement of the electrolyte.

**Pot Life:** The life of pots charged with Kalunite alumina appeared comparable to those charged with Bayer alumina. As an example, four pots were started on Kalunite alumina and at approximately the same time ten pots were started on Bayer alumina in pot room No. 1. They averaged 238 and 233 days of operation, respectively.

### Summary and Conclusions

The reduction of Kalunite alumina has produced commercially acceptable metal on a fairly large scale. While the operating record was not as favorable as for Bayer alumina, particularly with respect to current efficiency, it would appear that the operation will be controlled by economic conditions rather than technological consideration. Adverse effects of particle size were definitely confirmed. Improvement of the quality of Kalunite alumina with respect to chemical and physical properties, and/or modifying the electrolytic treatment will undoubtedly improve the reduction operation.

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\*\* Operation of the 10,000 amp furnace at Battelle Memorial Institute during 1940 was unsuccessful until coarse fractions were removed from the alumina feed by screening.

† The 10,000 amp cell operated at Battelle Memorial Institute showed a current efficiency of 85 pct.



# Intermetallic Compounds in the System Molybdenum-Beryllium

by Samuel G. Gordon, James A. McGurty, Gilbert E. Klein,  
and Walter J. Koshuba

ONE of the problems encountered in working with metals at elevated temperatures is the instability resulting from solid-solid diffusion at a common interface. A determination of the nature and magnitude of this phenomenon is important as related to structural properties of materials potentially useful in high temperature applications. This paper is concerned with the solid state reaction between metallic molybdenum and beryllium at elevated temperatures.

In the older literature,<sup>1</sup> there were no known intermetallic compounds in the system Be-Mo, and the list of beryllium intermetallics was rather small. New compilations have been made by Smithells<sup>2</sup> and by Taylor,<sup>3</sup> listing all the then known beryllium binary intermetallic compounds. In addition to these, some new phases have just been reported<sup>4</sup> in the system Zr-Be and some further compounds of the type  $\text{MBe}_{13}$  have been currently described.<sup>5</sup> The new compound  $\text{MoBe}_{13}$  which is reported upon in this paper differs considerably from the above mentioned  $\text{MBe}_{13}$  group, and will be discussed in detail.

## Diffusion Study

The nature of the solid diffusion at a Mo-Be interface was determined by sealing a beryllium rod inside a molybdenum capsule and heating at a temperature of 2000°F (1100°C) for 100 hr. The molybdenum capsule was fabricated from  $\frac{5}{8}$  in. swaged molybdenum rod obtained from the Fansteel Metallurgical Corp. The beryllium metal was obtained from Brush Beryllium Corp. as  $\frac{1}{4}$  in. cold-drawn rod. This material assayed 99.05 pct Be and contained as impurities 0.84 pct BeO and 0.19 pct  $\text{Be}_2\text{C}$ .

The molybdenum capsule was  $\frac{5}{8}$  in. in OD x 2 in. long. To prepare it, a concentric hole 0.250 in. + 0.001 in. — 0.000 in. in diam was drilled and reamed in one end of a rod to a depth of 1½ in. A 1 in. long beryllium rod 0.250 in. + 0.000 in. — 0.001 in. in diam was pressed into the molybdenum capsule. A molybdenum plug 0.250 in. ± 0.001 in. in diam x 9/16 in. long was then used to seal the beryllium in place. The capsules were placed in a molybdenum

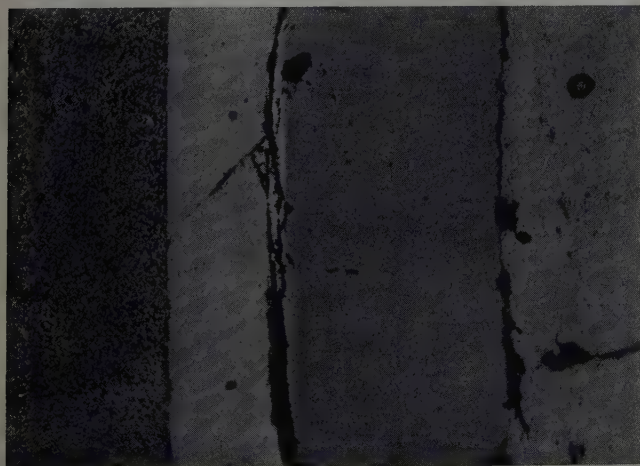


Fig. 1— $\text{MoBe}_2$  and  $\text{MoBe}_{13}$  formed by solid-solid reaction between Mo and Be at 1100°C (2012°F), polished section at X250, unetched.

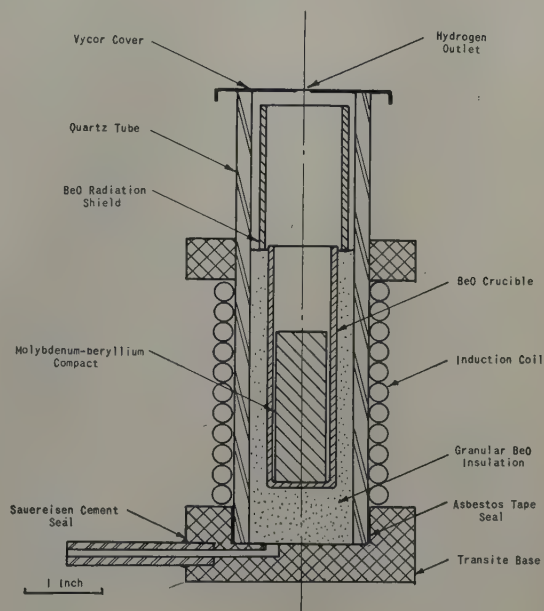


Fig. 2—Induction-heating melting assembly.

resistance furnace and heated at 2000°F (1100°C) for 100 hr. On cooling, the specimens were cut and examined metallographically. Fig. 1 is a micrograph at X250 of a portion of the interface from a transverse section. Four phases are clearly visible, with sharp boundaries between them. Phase A is a section of the molybdenum capsule; phase B is the molybdenum-rich intermetallic composition  $\text{MoBe}_2$ ; phase C is the beryllium-rich compound  $\text{MoBe}_{13}$ ; phase D is a section of the beryllium rod. All phases were readily polished to a high metallic luster.

The molybdenum-rich phase has a pronounced purple tinge. The beryllium-rich phase (C) is only slightly darker than the pure beryllium. In polarized reflected light, however, it shows striking birefringence between crossed Nicols. The black areas represent flaws or pores in the material. A small representative amount of powdered material from each of the phases was carefully removed under the microscope with a diamond tool. With this material, powder X-ray diffraction patterns were made for the identification of each phase. Table I lists the X-ray diffraction spacings and corresponding indexes characteristic of these intermetallic compounds.

## Synthesis

To establish the formula of the new intermetallic compound, X-ray diffraction patterns were made from powders obtained from solidified melts of known composition. The syntheses were made by

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Table I. Interplanar Spacings of Powdered Crystals

| Ni-filtered Cu radiation ( $K\alpha = 1.5418\text{\AA}$ ) |            |          |     |                    |            |          |     |
|-----------------------------------------------------------|------------|----------|-----|--------------------|------------|----------|-----|
| MoBe <sub>2</sub>                                         |            |          |     | MoBe <sub>13</sub> |            |          |     |
| hkl                                                       | Calculated | Observed | I*  | hkl                | Calculated | Observed | I*  |
| 10.0                                                      | 3.83       | 3.83     |     | 200                | 5.12       | 5.12     | 0.7 |
| 10.1                                                      | 3.37       | 3.37     |     | 111                | 4.02       | 4.02     |     |
| 10.2                                                      | 2.62       | 2.62     |     | 220                | 3.62       | 3.63     | 1.0 |
| 00.3                                                      | 2.52       | 2.54     |     | 300                | 3.37       | 3.37     | 0.1 |
| 11.0                                                      | 2.21       | 2.21     | 0.8 | 311                | 2.64       | 2.64     |     |
| 10.3                                                      | 2.06       | 2.05     | 1.0 | 400                | 2.56       | 2.56     | 0.9 |
| 20.0                                                      | 1.916      | 1.914    | 0.6 | 330                | 2.38       | 2.38     |     |
| 11.2                                                      | 1.885      | 1.884    |     | 401                | 2.21       | 2.21     | 0.2 |
| 00.4                                                      | 1.843      | 1.848    |     | 102                | 2.10       | 2.10     | 0.5 |
| 20.2                                                      | 1.695      | 1.692    |     | 500                | 2.05       | 2.05     | 0.3 |
| 20.3                                                      | 1.504      | 1.500    | 0.4 | 510                | 2.01       | 2.00     |     |
| 21.0                                                      | 1.450      | 1.450    |     | 212                | 1.952      | 1.954    | 0.2 |
| 21.1                                                      | 1.424      | 1.420    |     | 501                | 1.886      | 1.890    | 0.2 |
| 21.2                                                      | 1.356      | 1.360    | 0.5 | 222                | 1.840      | 1.840    |     |
| 20.4                                                      | 1.342      | 1.345    |     | 440                | 1.816      | 1.814    | 0.9 |
| 30.0                                                      | 1.280      | 1.279    | 0.3 | 600                | 1.700      | 1.701    | 0.1 |
| 21.3                                                      | 1.249      | 1.246    | 0.6 | 412                | 1.624      | 1.621    | 0.3 |
| 30.2                                                      | 1.206      | 1.206    | 0.3 | 601                | 1.555      | 1.552    | 0.3 |
| 20.5                                                      | 1.160      | 1.159    | 0.5 | 502                | 1.506      | 1.508    | 0.2 |
| 22.0                                                      | 1.107      | 1.109    | 0.3 | 700                | 1.460      | 1.453    | 0.1 |
| 31.0                                                      | 1.065      | 1.063    | 0.4 | 003                | 1.420      | 1.420    | 0.1 |
| 21.5                                                      | 1.030      | 1.028    | 0.5 | 213                | 1.365      | 1.368    | 0.4 |
| 31.3                                                      | 0.974      | 0.976    | 0.4 | 602                | 1.346      | 1.349    |     |
| 40.1                                                      | 0.951      | 0.952    |     | 313                | 1.322      | 1.326    | 0.1 |
| 40.2                                                      | 0.935      | 0.931    |     | 800                | 1.282      | 1.282    | 0.6 |
| 20.7                                                      | 0.908      | 0.906    |     | 403                | 1.250      | 1.247    | 0.3 |
| 40.3                                                      | 0.895      | 0.894    |     | 660                | 1.214      | 1.215    | 0.1 |
| 30.6                                                      | 0.888      | 0.887    |     | 702                | 1.210      | 1.209    |     |
| 23.0                                                      | 0.880      | 0.882    |     | 552                | 1.194      | 1.192    |     |
| 31.5                                                      | 0.859      | 0.861    |     | 503                | 1.176      | 1.179    |     |
| 21.7                                                      | 0.848      | 0.847    |     | 661                | 1.160      | 1.162    | 0.3 |
| 41.0                                                      | 0.838      | 0.840    |     | 513                | 1.150      | 1.153    | 0.3 |
| 41.1                                                      | 0.831      | 0.830    |     | 900                | 1.144      | 1.144    |     |
| 20.8                                                      | 0.825      | 0.824    | 0.6 | 443                | 1.110      | 1.109    | 0.2 |
| 22.6                                                      | 0.821      | 0.820    |     | 004                | 1.070      | 1.071    |     |
| 41.2                                                      | 0.818      | 0.818    | 0.6 | 204                | 1.050      | 1.048    | 0.2 |
| 31.6                                                      | 0.803      | 0.803    | 0.8 | 770                | 1.032      | 1.031    | 0.1 |
| 23.4                                                      | 0.795      | 0.793    |     | 1000               | 1.025      | 1.025    |     |
| 50.0                                                      | 0.772      | 0.773    |     | 304                | 1.010      | 1.010    | 0.2 |
|                                                           |            |          |     | 771                | 1.007      | 1.006    |     |
|                                                           |            |          |     | 005                | 0.978      | 0.977    | 0.2 |
|                                                           |            |          |     | 703                | 0.950      | 0.953    |     |
|                                                           |            |          |     | 1100               | 0.935      | 0.933    |     |
|                                                           |            |          |     | 444                | 0.925      | 0.923    |     |
|                                                           |            |          |     | 880                | 0.914      | 0.914    | 0.4 |
|                                                           |            |          |     | 604                | 0.910      | 0.908    |     |
|                                                           |            |          |     | 881                | 0.885      | 0.887    |     |

\* Relative intensities are given where they are 0.1 or greater.

melting Mo-Be mixtures in various stoichiometric proportions.

A high purity molybdenum powder averaging 2 to 5 microns in particle size was obtained from the Fansteel Metallurgical Corp. A beryllium metal 200 mesh powder was obtained from the Brush Beryllium Corp. The material assayed 99.5 pct Be and contained as impurities 0.63 pct BeO, 0.12 pct Al, 0.12 pct Fe, and 0.04 pct Be<sub>3</sub>C. Powder mixtures of the two elements were ball milled in a rubber-lined mill using rubber-covered steel balls; the mixtures were then mechanically compressed at 100,000 psi into compacts which were approximately 2 in. long x 5/8 in. diam. These compacts were melted directly by induction. Fig. 2 is a schematic drawing of the melting assembly. A 20 kw Ajax induction unit permitted rapid heating to 3092° to 3272°F (1700° to 1800°C) in which temperature range all the compositions investigated were liquid.

On heating the unsintered compacts, an exothermic reaction was noted in the range 1472° to 1832°F (800° to 1000°C), due perhaps to a solid-solid reaction between the molybdenum and beryllium. The

Table II. Unit Cell Constants (MoBe<sub>2</sub>)<sub>4</sub>

|                                    | NEPA          | Taylor |
|------------------------------------|---------------|--------|
| $\alpha_0$                         | 4.433Å        | 4.434Å |
| $\alpha_0\sqrt{3}/2$               | 3.838         |        |
| $c_0$                              | 7.341Å        | 7.275Å |
| $Z$                                | 4             | 4      |
| $\rho$                             | 6.06          | 6.13   |
| Density                            | 5.92 g per cc |        |
| Space group $D_{6h}^{14}$ —C6/mmc. |               |        |

liquid melt was held at a temperature of 3092° to 3272°F (1700° to 1800°C) for 10 min and then was allowed to cool in the crucible. The solid button readily separated from the crucible with little surface adherence. X-ray powder patterns were made of representative specimens from each melt. Comparison of these patterns with the standards for the two phases B and C showed that the composition corresponding to MoBe<sub>2</sub> was identifiable as the molybdenum-rich phase (B). The beryllium-rich phase was found to be MoBe<sub>13</sub>.

### Crystallographic Investigation

Well developed single crystals of the intermetallic compounds up to one millimeter in size were recovered from aggregates found in the ingots prepared for X-ray identification work. By careful mounting of these single crystals on a two-circle goniometer, oriented specimens were prepared suitable for use with a Weissenberg camera, using Ni-filtered Cu radiation ( $K\alpha = 1.5418\text{\AA}$ ) and with a precession X-ray camera. Measurements of the resulting X-ray diffraction patterns made possible the determination of unit cell constants of both intermetallic compounds. The density of single crystals of the relatively heavy MoBe<sub>2</sub> was measured by pycnometric methods using toluene. The density of MoBe<sub>13</sub> was measured using the float or sink method with Clerici solution and subsequently determining pycnometrically the density of the solution in which the crystal neither sinks nor floats.

MoBe<sub>2</sub>, the molybdenum-rich phase, occurred as parallel growths of tabular hexagonal crystals which showed the purple tinge characteristic of this phase. The unit cell constants determined from the diffraction pattern measurements are compared with values reported by Taylor<sup>2,6</sup> in Table II.

MoBe<sub>13</sub>, the new beryllium-rich phase occurred as aggregates of prismatic tetragonal crystals. Single crystal measurements yielded the following constants:  $a_0$ , 10.27Å;  $a_0\sqrt{2}$ , 14.52;  $c_0$ , 4.29Å;  $Z$ , 4;  $\rho$ , 3.13; and density, 3.13 g per cc. Since there were no systematic extinctions, the following space groups were possible: P42m, P4/m, or P42. Considerations of placing the 56 atoms (4 Mo and 52 Be) and of evidence obtained by Laue techniques indicate the space group P42 as being the most probable. The formula (MoBe<sub>13</sub>)<sub>4</sub> was calculated from the unit cell dimensions and the measured density.

### Conclusions

1—The existence of the intermetallic compound MoBe<sub>2</sub> has been verified. A table of the interplanar spacings of this compound is given.

2—A new intermetallic compound, MoBe<sub>13</sub>, is reported. This differs from other intermetallic compounds of the type MB<sub>13</sub> in being tetragonal instead of cubic. A table of the interplanar spacings of this compound is also included.

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# Thermal Stability of The Chromium, Iron, and Tungsten Borides In Streaming Ammonia And The Existence of a New Tungsten Nitride

by R. Kiessling and Y. H. Liu

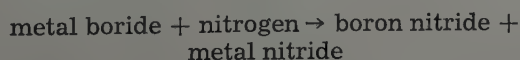
The chromium, iron, and tungsten borides have been treated with ammonia at different temperatures. They are attacked, forming metal nitride and boron nitride, and the results are summarized in the tables. In the tungsten-nitrogen system a new phase has been observed, closely related to the known  $\beta$  phase.

THE present investigations were begun to determine whether any ternary phases exist in the transition metal-boron-nitrogen systems for the metals chromium, iron, and tungsten. Attempts to prepare such phases were made by using the borides of the metals as starting materials and ammonia as the nitriding agent. Although no new ternary phases have been found to exist, the results may be of some interest with regard to the technical use of the borides.

## General Procedure

A steady stream of dry ammonia was passed through a silica reaction tube, the central part of which was kept at the reaction temperature while its ends were water-cooled. Weighed amounts of the borides were placed in a silica or porcelain boat and heated at different temperatures for a period of 10 to 24 hr. The boat was then rapidly removed from the reaction zone to the quenching zone, the water-cooled end of the tube, by means of a simple magnetic device. The nitrogen content of the products was determined by the increase in weight of the specimens, and the phase analysis was carried out by X-ray methods. For this analysis a Guinier-type camera, constructed at this Institute, was used with a bent, ground quartz crystal monochromator.

The general reaction, which occurred in all the experiments, may be summarized as:



For the higher temperatures pure metal was formed instead of metal nitride. It is sometimes difficult to

detect boron nitride among the reaction products by X-ray methods. Prolonged exposures of some specimens showed, however, that the strongest reflections of boron nitride were present. Additional evidence for its presence was given by the increase in weight of the specimens after nitriding. This increase was always greater than that corresponding to nitride formation only and was often in close agreement with the formula given above. Finally, a white powder, which was shown by X-ray methods to be boron nitride, was left if the reaction products after nitriding  $\text{Fe}_2\text{B}$  at  $448^\circ\text{C}$  and  $\text{FeB}$  at  $768^\circ\text{C}$  were dissolved in diluted sulphuric acid.

## Chromium-Boron-Nitrogen

Five phases have been found to exist in the Cr-B system,<sup>1, 2</sup> and all were used as starting materials. Investigations on the Cr-N system have shown the existence of two nitrides with ideal composition  $\text{Cr}_2\text{N}$  and  $\text{CrN}$ .<sup>3, 4</sup> The results are summarized in Table I. All the borides are attacked and decomposed into chromium nitride and boron nitride, and the kind of nitride formed depends only on the temperature and not on the boride used as starting material. The lowest reaction temperature, however, is different for the different borides. Thus the  $\delta$  phase begins to react at about  $735^\circ\text{C}$ , the  $\epsilon$  phase at about  $800^\circ$ , the  $\zeta$  phase at about  $900^\circ$ , the  $\eta$  phase

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Table I. Phases Present After Nitriding of the Chromium Borides in a Dry Ammonia Stream for 10 Hr. All Specimens Quenched from the Reaction Temperature. The Phases Present after Nitriding Have Been Placed in Order of Decreasing Amount in This and the Following Tables Except for Boron Nitride, which Always Has Been Placed Last.

| Temperature,<br>°C | Initial Chromium Boride                        |                                                |                                                |                                        |                                   |
|--------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|----------------------------------------|-----------------------------------|
|                    | $\delta$<br>( $\sim\text{Cr}_2\text{B}$ )      | $\epsilon$<br>( $\text{Cr}_3\text{B}_2$ )      | $\zeta$<br>( $\text{CrB}$ )                    | $\eta$<br>( $\text{Cr}_3\text{B}_4$ )  | $\theta$<br>( $\text{CrB}_2$ )    |
| 552                | $\text{Cr}_2\text{B}$                          | $\text{Cr}_3\text{B}_2$                        | $\text{CrB}$                                   | $\text{Cr}_3\text{B}_4$                | $\text{CrB}_2$                    |
| 735                | $\text{Cr}_2\text{B} + \text{CrN} + \text{BN}$ | $\text{Cr}_3\text{B}_2$                        | $\text{CrB}$                                   | $\text{Cr}_3\text{B}_4$                |                                   |
| 800                | $\text{CrN} + \text{Cr}_2\text{N} + \text{BN}$ | $\text{Cr}_3\text{B}_2 + (\text{CrN})$         | $\text{CrB}$                                   | $\text{Cr}_3\text{B}_4$                | $\text{CrB}_2$                    |
| 900                |                                                | $\text{CrN} + \text{Cr}_2\text{N} + \text{BN}$ | $\text{CrB} + (\text{CrN})$                    | $\text{Cr}_3\text{B}_4$                |                                   |
| 954                | $\text{CrN} + \text{Cr}_2\text{N} + \text{BN}$ |                                                |                                                |                                        | $\text{CrB}_2$                    |
| 1000               |                                                | $\text{CrN} + \text{Cr}_2\text{N} + \text{BN}$ | $\text{CrB} + \text{CrN} + \text{BN}$          |                                        | $\text{CrB}_2$                    |
| 1050               | $\text{CrN} + \text{Cr}_2\text{N} + \text{BN}$ |                                                | $\text{CrN} + \text{Cr}_2\text{N} + \text{BN}$ | $\text{CrN} + \text{Cr}_3\text{B}_4 +$ | $\text{CrB}_2 + \text{CrN}$       |
| 1100               |                                                |                                                |                                                | $(\text{Cr}_2\text{N}) + \text{BN}$    |                                   |
| 1180               | $\text{Cr}_2\text{N} + \text{BN}$              | $\text{Cr}_2\text{N} + \text{BN}$              | $\text{Cr}_2\text{N} + \text{BN}$              | $\text{Cr}_2\text{N} + \text{BN}$      | $\text{Cr}_2\text{N} + \text{BN}$ |

The lattice parameters found for the nitrides were:

$\text{CrN}$ :  $a = 4.150$  to  $4.145\text{\AA}$  (Blix;  $a = 4.148\text{\AA}$ )

$\text{Cr}_2\text{N}$ :  $a = 4.805$  to  $4.786$ ,  $c = 4.480$  to  $4.463\text{\AA}$ \*

(Eriksson:  $a = 4.806$  to  $4.760\text{\AA}$   
 $c = 4.479$  to  $4.438\text{\AA}$ )

No change in lattice parameters was observed for the borides.

\* Depending on temperature.

between  $900^\circ$  and  $1000^\circ$ , and the  $\theta$  phase at about  $1000^\circ\text{C}$ . It is of interest to note that this increase in stability bears a relationship to the crystal structures of the borides. The boron atoms in the  $\delta$  phase are only in contact with metal atoms, but not with any other boron atoms.\* The structure of the  $\epsilon$  phase is not known; but in the  $\zeta$  phase the boron atoms form chains; in the  $\eta$  phase, double chains; and in the  $\theta$  phase, hexagonal nets. The boron atoms thus form an increasing number of boron-boron bonds with increasing boron content of the phases, and the lower temperature limit where reaction occurs also seems to increase with the number of bonds. The dimensions of the chromium nitrides formed during the reactions are very similar to those reported in the literature, Table I. As the radius of boron is considerably greater than that of nitrogen this indicates that the nitrides formed do not contain any boron.

### Iron-Boron-Nitrogen

Both the  $\text{Fe-B}^{7,8}$  and the  $\text{Fe-N}^{7,8}$  systems have been investigated. The two iron borides,  $\text{Fe}_2\text{B}$  and  $\text{FeB}$ , were used as starting materials, and the results are summarized in Table II. The lowest temperature

Table II. Phases Present after Nitriding of the Iron Borides in a Dry Ammonia Stream for 24 hr. All Specimens Were Quenched from the Reaction Temperature

| Temperature,<br>°C | Initial Iron Boride                                  |                                                    |
|--------------------|------------------------------------------------------|----------------------------------------------------|
|                    | $\text{Fe}_2\text{B}$                                | $\text{FeB}$                                       |
| 352                | $\text{Fe}_2\text{B}$                                | $\text{FeB}$                                       |
| 400                | $\zeta + \text{BN}$                                  | $\text{FeB} + \zeta + \text{BN} (?)$               |
| 448                | $\epsilon + \text{BN}$                               |                                                    |
| 505                | $\epsilon + \gamma' + \text{BN}$                     |                                                    |
| 550                | $\gamma' + \epsilon + \text{BN}$                     | $\gamma' + \epsilon + \text{BN}$                   |
| 602                | $\alpha\text{Fe} + \gamma' + (\epsilon) + \text{BN}$ | $\gamma' + \epsilon + \alpha\text{Fe} + \text{BN}$ |
| 702                | $\alpha\text{Fe} + \text{BN}$                        |                                                    |
| 768                | $\alpha\text{Fe} + \text{BN}$                        | $\alpha\text{Fe} + \text{BN}$                      |

The Greek letters denote the nitrides of iron according to Hägg's notation. The lattice parameters found for the different nitrides were:

$\zeta$ :  $a = 2.758$ ,  $b = 4.777$ ,  $c = 4.416$  (Jack:  $a = 2.763 - 2.761$ ,  
 $b = 4.828 - 4.830$ ,  
 $c = 4.425\text{\AA}$ )

$\epsilon$ :  $a = 2.714$  to  $2.748$ ,  $b = 4.701$  to  $4.760$ ,  $c = 4.381$  to  $4.409^*$   
(Jack:  $a = 2.764$ ,  
 $b = 4.787$ ,  
 $c = 4.420\text{\AA}$ )

$\gamma'$ :  $a = 3.789$  to  $3.795\text{\AA}$ \* (Jack:  $a = 3.794\text{\AA}$ )

$\alpha\text{Fe}$ :  $a = 2.867\text{\AA}$

No change in lattice parameters was observed for the borides.

\* Depending on temperature.

at which reaction occurs seems to be lower for  $\text{Fe}_2\text{B}$  (isolated boron atoms) than for  $\text{FeB}$  (boron chains). The products of the reaction are boron nitride and those iron nitrides which are stable in streaming ammonia at the reaction temperature. Thus the same tendency is shown by the iron borides as by the chromium borides. The borides seem to be more stable if the boron atoms are forming boron-boron bonds than if they are isolated, but the difference is not so marked in this system. The dimensions of the unit cells of the iron nitrides and iron formed in the reactions are in close agreement with those reported in the literature, Table II. Therefore the nitrides formed in this system do not seem to contain any boron either.

### Tungsten-Boron-Nitrogen

The three known tungsten borides<sup>9</sup> were used as starting materials. Investigations on the W-N system<sup>10</sup> have shown the existence of one nitride of probable composition  $\text{W}_2\text{N}$ , called the  $\beta$  phase. The results of nitriding are summarized in Table III. In specimens nitrided between  $825^\circ$  and  $875^\circ\text{C}$ , lines of a new phase appeared, which has not been described before. This phase was also found when pure tungsten was nitrided. It was called the  $\gamma$  phase in the W-N system and will be discussed below.

The marked increase in stability of the borides with increasing number of boron-boron bonds, which was noted for the chromium and the iron borides, is not found in this system. All of them begin to be attacked at temperatures between  $800^\circ$  and  $900^\circ\text{C}$ . The parameter of the cubic  $\beta$ -tungsten nitride was found to agree with that reported in the literature, indicating that the nitride is free from interstitial boron in the lattice.

### $\gamma$ Phase, Tungsten-Nitrogen

Earlier investigations on the W-N system have shown the existence of one tungsten nitride, slowly formed by nitriding tungsten with ammonia between  $700^\circ$  and  $800^\circ\text{C}$ .<sup>10</sup> It has not been possible to obtain this phase, called the  $\beta$  phase and assumed to have the composition  $\text{W}_2\text{N}$ , in a pure state. It

\* As a result of a renewed study of the  $\delta$  phase in the Cr-B system there is reason to suppose that it has the same structure as the  $\delta$  phase in the Mn-B system, where boron-boron contacts do not appear. In an earlier study,<sup>2</sup> one of the present authors (R. Kiessling) suggested that there is a slight difference between the structures of these two phases. This assumption was based on differences between rotation and Weissenberg photographs which seem to have been caused by twinning of the crystals of the Cr-B phase.



Table III. Phases Present After Nitriding of Tungsten and the Tungsten Borides in a Dry Ammonia Stream for 10 Hr. All Specimens Were Quenched from the Reaction Temperature.

| Temperature,<br>°C | Initial Tungsten Boride  |                                                  |                                    |                                                 |
|--------------------|--------------------------|--------------------------------------------------|------------------------------------|-------------------------------------------------|
|                    | W                        | W <sub>2</sub> B                                 | "WB"                               | WB <sub>2</sub>                                 |
| 700                | $\alpha$ W + ( $\beta$ ) | W <sub>2</sub> B                                 | WB                                 | WB <sub>2</sub>                                 |
| 750                | $\alpha$ W + $\beta$     | W <sub>2</sub> B                                 | WB                                 | WB <sub>2</sub>                                 |
| 800                | $\alpha$ W + $\beta$     | W <sub>2</sub> B                                 | WB + (W + $\beta$ + BN)            |                                                 |
| 825                | $\alpha$ W + $\gamma$    |                                                  |                                    |                                                 |
| 850                | $\alpha$ W + $\gamma$    | W <sub>2</sub> B + $\alpha$ W + ( $\gamma$ + BN) | $\alpha$ W + WB + ( $\gamma$ + BN) | $\alpha$ W + WB <sub>2</sub> + ( $\gamma$ + BN) |
| 875                | $\alpha$ W + $\gamma$    |                                                  |                                    |                                                 |
| 900                | $\alpha$ W               | $\alpha$ W + W <sub>2</sub> B + BN               | $\alpha$ W + (WB) + BN             | $\alpha$ W + (WB <sub>2</sub> ) + BN            |
| 1000               | $\alpha$ W               | $\alpha$ W + (W <sub>2</sub> B) + BN             | $\alpha$ W + BN                    |                                                 |
| 1100               |                          | $\alpha$ W + BN                                  |                                    | $\alpha$ W + BN                                 |

$\beta$  and  $\gamma$  denote the known nitride "W<sub>2</sub>N" and the new nitride, respectively.  
The lattice parameters were found to be:  
 $\beta$  :  $a = 4.128\text{\AA}$  (Hägg :  $a = 4.126\text{\AA}$ )  
 $\gamma$  :  $a = 4.130$  to  $4.122\text{\AA}$   
 $\alpha$ W :  $a = 3.164\text{\AA}$   
No change in lattice parameters was observed for the borides.

\*Depending on nitriding temperature.

always appears mixed with tungsten. The crystal structure is that of a face-centered cubic metal lattice with four atoms in the unit cell and a parameter of  $a = 4.126\text{\AA}$ . On nitriding tungsten with ammonia at temperatures between 825° and 875°C, the quenched specimens showed lines of a new phase, called the  $\gamma$  phase by the present authors, Tables III and IV. Its lattice is probably closely related to that of the  $\beta$  phase, see below. The  $\gamma$  phase always appeared mixed with tungsten, and it was thus not possible to determine its nitrogen content. It probably has a composition close to that of the  $\beta$  phase (ideal composition W<sub>2</sub>N), as the increase in weight of tungsten was about the same when the  $\beta$  phase was formed as when the  $\gamma$  phase was formed (1.6 pct). Some heat treatments were carried out in order to study the thermal stability of the  $\gamma$  phase and the relationship between the  $\beta$  and  $\gamma$  phases. The  $\beta$  phase, formed at 750°C, was transformed to the  $\gamma$  phase on heating in a stream of ammonia at 850°C for 10 hr. The  $\gamma$  phase formed at 850°C was decomposed into tungsten and nitrogen on heating at 900°C in ammonia or in evacuated silica tubes. All attempts to transform the  $\gamma$  to the  $\beta$  phase, however, were unsuccessful. The  $\gamma$  phase was, for instance, heated at 700°, 760°, and 800°C for times up to 36 hr in streaming ammonia or at the same temperatures in evacuated silica tubes for times up to 24 hr, but no change was observed. It is thus impossible to decide from these experiments, whether the  $\gamma$  phase is a high temperature phase which transforms only very slowly to the  $\beta$  phase at lower temperatures, or a stable phase formed with the maximum velocity in streaming ammonia between 825° and 875°C, but the former possibility is the most probable.

X-ray investigations show that the  $\gamma$  phase gives reflections attributable to a simple cubic lattice. The length of the unit cell axis varies between the limits  $a = 4.130\text{\AA}$  at 825°C and  $a = 4.122\text{\AA}$  at 875°C, indicating an extended homogeneity range. All the reflections from a simple cubic lattice were present, but those with unmixed indexes were appreciably stronger than those with mixed indexes. This indicates a close relationship between the face-centered  $\beta$  phase, which only gives reflections with unmixed indexes and an axis of  $a = 4.126\text{\AA}$ , and this new  $\gamma$  phase.

The authors have assumed that the products after nitriding at 825° to 875°C consist of two phases,

tungsten and the new  $\gamma$  nitride. There is also a possibility that a mixture of three phases exists, namely tungsten,  $\gamma$  nitride, and  $\beta$  nitride, and that some of the reflections from the  $\beta$  and  $\gamma$  phases coincide. This assumption is not very probable, however, as all the reflections fit exactly into the same quadratic form. In addition, there is no indication of any extended homogeneity range of the  $\beta$  phase which would have to exist if some of the reflections of the  $\beta$  and  $\gamma$  phases were always to coincide. All the reflections from the nitride formed between 825° and 875°C therefore have been assumed to belong to one phase alone, the new  $\gamma$  phase.

The new reflections are much too strong to be considered as due only to an ordered distribution of the nitrogen atoms of the  $\beta$  phase. Consequently, the metal lattice must be deformed so that the face-centering disappears. Such a deformation may be caused by an ordering of the nitrogen atoms or by a change in the nitrogen content. The  $\gamma$  phase thus might be regarded as analogous to the  $\beta$  phase in the Mo-N° and the  $\delta$  phase in the Mn-N<sup>11</sup> systems. They are both high temperature phases, closely related to the face-centered cubic phases in the Mo-N ( $\gamma$ ) and Mn-N ( $\epsilon$ ) systems, respectively, and are formed by a tetragonal deformation of the face-centered metal lattices.

An attempt to determine the crystal structure of

Table IV. Tungsten-Nitrogen System. Powder Diffraction Lines of the  $\gamma$  Phase Quenched from 875°C. Cu-K <sub>$\alpha$</sub>  Radiation.

| I | sin <sup>2</sup> $\theta$ | $a = 4.122$ | $a = 16.488$ | I  | sin <sup>2</sup> $\theta$ | $a = 4.122$ | $a = 16.488$ |
|---|---------------------------|-------------|--------------|----|---------------------------|-------------|--------------|
|   |                           | hkl         | hkl          |    |                           | hkl         | hkl          |
| w | 0350                      | 100         | 200          | w  | 4546                      | 320         | 640          |
| w | 0706                      | 110         | 220          | m  | 4736                      | $\alpha$ W  |              |
| s | 1050                      | 111         | 222          | w  | 4898                      | 321         | 642          |
| s | 1190                      | $\alpha$ W  |              | w  | 5579                      | 400         | 800          |
| s | 1395                      | 200         | 400          | s* | 5922                      | $\alpha$ W  |              |
| w | 1750                      | 210         | 420          | w  | 6291                      | 330         | 822          |
| w | 2097                      | 211         | 422          | m  | 6624                      | 331         | 660          |
| s | 2374                      | $\alpha$ W  |              | m  | 6973                      | 420         | 840          |
| m | 2788                      | 220         | 440          | m  | 7114                      | $\alpha$ W  |              |
| w | 3134                      | 300         | 600          | s  | 8295                      | $\alpha$ W  |              |
|   |                           |             | 442          | w  | 8347                      | 422         | 844          |
| w | 3489                      | 310         | 620          | w  | 8720                      | 500         | 1000         |
| s | 3552                      | $\alpha$ W  |              |    |                           |             | 860          |
| m | 3825                      | 311         | 622          | w  | 9078                      | 510         | 1020         |
|   |                           |             |              |    |                           |             | 862          |
| w | 4188                      | 222         | 444          | w  | 9417                      | 333         | 1022         |
|   |                           |             |              |    |                           |             | 666          |

w, weak; s, strong; m, medium.

\* 410 (resp. 820 + 644) coincide with 310 from  $\alpha$ -tungsten.

Table V.  $\gamma$  Phase, Quenched from 875°C.Structure factor values for the limits of the parameter ( $x$ ) in 4: (e), space group  $P23$  or  $P43m$  for some reflections.

| $hkl$ | $A^2$ for $x =$ |      |       | $I$ ,<br>Obs. |
|-------|-----------------|------|-------|---------------|
|       | 0.23            | 0.25 | 0.27  |               |
| 100   | 0.24            | 0    | 0.24  | 50            |
| 110   | 0.004           | 0    | 0.004 | 50            |
| 200   | 15.3            | 16   | 15.3  | 250           |

the new phase was not successful. If it is assumed to have four tungsten atoms per unit cell, which is very probable because of the close correspondence in dimensions between the  $\beta$  and  $\gamma$  phase, and a simple cubic lattice, only the space groups  $Pm3$ ,  $P23$ ,  $Pm3m$ ,  $P43$ , and  $P43m$  are possible. Four metal atoms forming a noncentered lattice can only be placed in these space groups in the fourfold positions 4: (e) in  $P23$  and  $P43m$ . They both give the same arrangement with the coordinates  $xxx$ ;  $\bar{x}\bar{x}\bar{x}$ ;  $\bar{x}\bar{x}\bar{x}$ ;  $xxx$ . For  $x = 1/4$  a face-centered lattice is obtained, and from space considerations ( $r_w > 1.34$ ) it is easily seen that the limits for the parameter are  $0.23 < x < 0.27$ . A study of the structure factors shows that this arrangement is not in agreement with the observed intensities, Table V. The possibility of a cubic unit cell with an axis of  $a_1 = 2a$  or  $a_1 = 3a$  must be excluded as some observed lines then correspond to numbers in the quadratic form which are not sums of squares of integers (28 in the former case, 15, 39, and 60 in the latter). A unit cell with an axis of  $a_1 = 4a$  is again possible, however, and the indexes of this bigger cell are also given in Table IV. The probable space groups for this cell are  $Fm3c$ ,  $F43c$ ,  $Fm3$ , and  $F23$ . The structure of the metal lattice must be closely related to that formed by 64 face-centered cubic cells, each with  $a = 4.130$  to  $4.122\text{\AA}$  and four metal atoms per unit cell. It is possible to place 256 atoms in positions corresponding to such a structure in the space groups mentioned, but the task of varying the parameters in a systematic way to obtain a deformed structure giving the observed intensities is too difficult when only powder data are available.

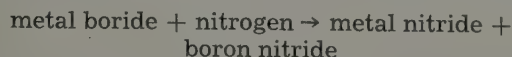
The symmetry might also be tetragonal or still lower. No indication of splitting up the reflections was observed, however, and thus the ratio  $c/a$  must be equal or nearly equal to an integer. This case, although possible, is not very plausible.

The possibilities of a defect lattice with missing tungsten atoms or a lattice where tungsten atoms are replaced by nitrogen atoms are not conceivable.

Summing up the different possibilities discussed, the most probable, in the opinion of the authors, is a cubic cell containing 256 tungsten atoms with positions nearly corresponding to a cubic close-packing.

### Discussion

The present results indicate that the formation of boron nitride is a deceivable factor in the reaction:



Boron nitride is a very stable compound with a high melting point. Its lattice is similar to that of graphite, consisting of hexagonal nets where each boron atom within a net is in contact with three nitrogen atoms and each nitrogen atom with three

boron atoms. A B-N pair has the same number of electrons as two carbon atoms and the nets are probably formed by strong resonating B-N bonds. The fact that the stability of the chromium and iron borides in ammonia increases with increasing number of boron-boron contacts is of interest and supports the assumption that strong boron-boron bonds exist in the higher borides.

It is also of interest to note that the  $\delta$  phase in the Cr-B system is attacked at a considerably higher temperature than  $\text{Fe}_2\text{B}$ , and that the  $\zeta$  phase in the Cr-B system is more stable against attack than  $\text{FeB}$ . Although  $\delta$  Cr-B and  $\text{Fe}_2\text{B}$ , as well as  $\zeta$  Cr-B and  $\text{FeB}$ , are not isomorphous, their structures are closely related and the results consequently support the view that the strength of the metal-boron bond decreases with increasing atomic number of the transition element in the same period. This decrease has also been noted for the metal-hydrogen, metal-carbon, and metal-nitrogen bonds. The stability of hydrides, carbides, and nitrides decreases with increasing atomic number of the transition element in a period.

### Summary

The borides of chromium, iron, and tungsten have been treated with ammonia at different temperatures. They are all attacked and form metal nitride and boron nitride. For the chromium and iron borides, the stability in ammonia increases with increasing boron content, which supports the view that strong boron-boron bonds exist in the higher borides.

In the W-N system a new phase ( $\gamma$ ) has been observed. It is formed at nitriding temperatures between 825° and 875°C and is probably closely related to the already known  $\beta$  phase. All the reflections observed may be interpreted assuming a cubic cell with  $a = 4.130$  to  $4.122\text{\AA}$  (depending on nitriding temperature) and containing 4 tungsten atoms. There are reasons to assume that the real unit cell of this phase is cubic and contains 256 tungsten atoms (cube edge =  $4a$ ) in positions nearly corresponding to a cubic close-packing.

The investigations also support the view that the strength of the metal-boron bond decreases with increasing atomic number of the transition metal in the same period.

### Acknowledgment

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# Effect of Alloying Elements on the Elevated Temperature

## Plastic Properties of Alpha Solid Solutions of Aluminum

by O. D. Sherby, R. A. Anderson, and J. E. Dorn

Solid solution alloying increases the plastic properties of aluminum at elevated temperatures by solid solution strengthening, by restraining recovery and recrystallization, and by a Cottrell effect. When binary aluminum alloys are strained and aged at 194° to 300°K they develop a yield point. This is attributed to a migration of dislocations to solute atoms during aging.

IN view of the ever expanding interest in applications of metals and alloys to high temperature service conditions, it becomes increasingly important to be cognizant of the effect of various metallurgical factors on the strength of alloys at elevated temperatures. One problem of wide interest, not only because of its engineering significance but also due to its fundamental scientific importance, is the elucidation of the effect of alloying elements on the plastic properties of homogeneous  $\alpha$  solid solutions at elevated temperatures. It is indeed astonishing to note that in spite of its importance, and in spite of extensive random testing of alloys at elevated temperatures, no systematic investigation has been reported yet on the effect of alloying additions on the plastic properties of  $\alpha$  solid solutions at elevated temperatures. This deficiency in our knowledge prompted the investigation described in this report.

Rather extensive data are currently available on the effect of alloying elements on the plastic properties of  $\alpha$  solid solutions at atmospheric and sub-atmospheric temperatures. Such data might be ex-

trapolated to higher temperatures and reasonable guesses might be made regarding the influence of such factors as recovery and recrystallization in order to hazard a qualitative estimate of the effect of alloying elements on the plastic properties of  $\alpha$  solid solutions at elevated temperatures. Such

Table I. Chemical Analyses and Grain Size of Alloys

| Alloy-<br>ing<br>Element | Atomic<br>Pct | Grain<br>Size<br>Diam,<br>mm | Chemical Analyses<br>(Wt Pct Impurities) |       |       |        |       |
|--------------------------|---------------|------------------------------|------------------------------------------|-------|-------|--------|-------|
|                          |               |                              | Si                                       | Fe    | Cu    | Mg     | Mn    |
| Al                       | 0             | 0.21                         | 0.003                                    | 0.003 | 0.006 | 0.001  |       |
| Mg                       | 0.554         | 0.25                         | 0.003                                    | 0.003 | 0.007 |        |       |
|                          | 1.097         | 0.28                         | 0.004                                    | 0.004 | 0.007 |        |       |
|                          | 1.617         | 0.26                         | 0.003                                    | 0.004 | 0.006 |        |       |
|                          | 3.228         | 0.27                         | 0.003                                    | 0.004 | 0.007 |        |       |
| Cu                       | 0.029         | 0.29                         | 0.003                                    | 0.004 |       | 0.0006 | 0.001 |
|                          | 0.054         | 0.29                         | 0.003                                    | 0.004 |       | 0.0007 | 0.001 |
|                          | 0.101         | 0.29                         | 0.003                                    | 0.003 |       | 0.0006 | 0.001 |
|                          | 0.233         | 0.30                         | 0.003                                    | 0.004 |       | 0.0006 | 0.001 |
| Zn                       | 0.211         | 0.26                         | 0.004                                    | 0.004 | 0.006 | 0.001  |       |
|                          | 0.402         | 0.27                         | 0.004                                    | 0.005 | 0.006 | 0.001  |       |
|                          | 0.755         | 0.26                         | 0.004                                    | 0.005 | 0.006 | 0.001  |       |
|                          | 1.616         | 0.26                         | 0.003                                    | 0.005 | 0.007 | 0.001  |       |
| Ge                       | 0.015         | 0.27                         | 0.004                                    | 0.004 | 0.006 | 0.001  |       |
|                          | 0.033         | 0.26                         | 0.004                                    | 0.004 | 0.006 | 0.001  |       |
|                          | 0.082         | 0.27                         | 0.003                                    | 0.005 | 0.007 | 0.001  |       |
|                          | 0.145         | 0.26                         | 0.003                                    | 0.006 | 0.007 | 0.001  |       |
| Ag                       | 0.025         | 0.31                         | 0.003                                    | 0.005 | 0.006 | 0.001  |       |
|                          | 0.053         | 0.29                         | 0.003                                    | 0.005 | 0.006 | 0.001  |       |

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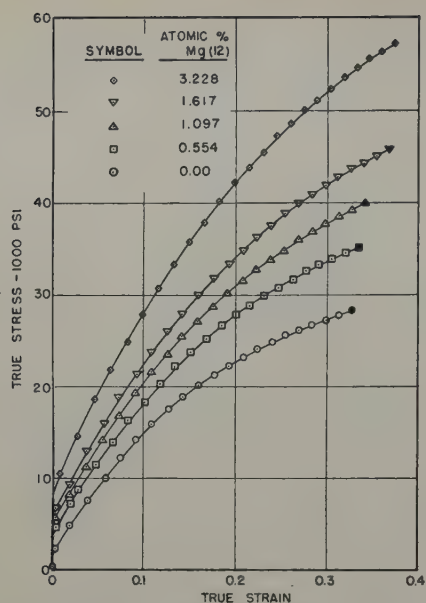


Fig. 1—Effect of magnesium on the work hardening of aluminum at 78°K.

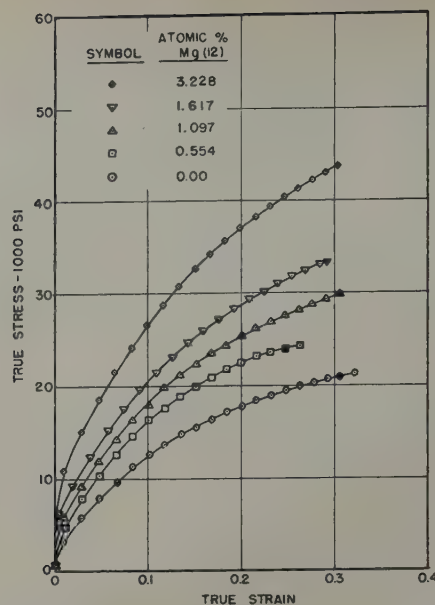


Fig. 2—Effect of magnesium on the work hardening of aluminum at 116°K.

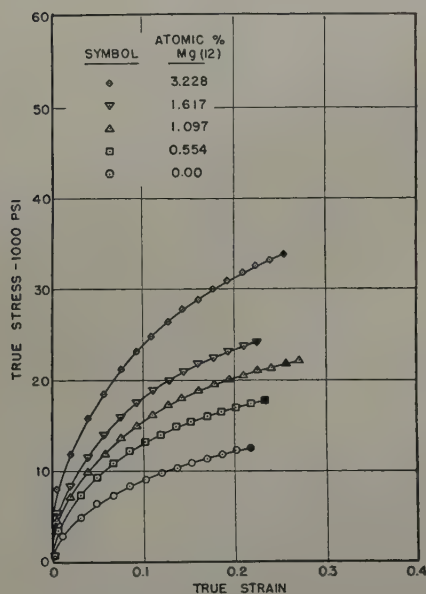


Fig. 3—Effect of magnesium on the work hardening of aluminum at 194°K.

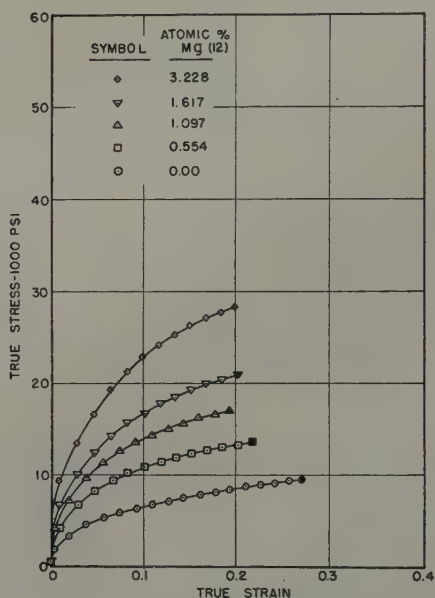


Fig. 4—Effect of magnesium on the work hardening of aluminum at 293°K.

guesses would indicate the recognized factors of importance in the plastic properties of homogeneous alloys at elevated temperatures and would prescribe the interesting variables to be considered in studying the problem more thoroughly. If such guesses prove to be fairly accurate the need for detailed research on the elevated temperature plastic properties will be much reduced.

It is quite possible, however, that other factors, not so widely recognized, may also prove to be important in affecting the elevated temperature plastic properties of alloys. The following investigation was therefore undertaken in order to evaluate more completely the effect of various factors on the solid solution strengthening of alloys at elevated temperatures. Aluminum was selected as the solvent in view of the extensive correlatable data now available on its plastic properties at low temperatures.<sup>1</sup> The general principles uncovered in this investiga-

tion, however, are probably applicable to other systems using higher melting solvents.

### Materials and Method

The compositions and grain sizes of the alloys used in this investigation are given in Table I. Each alloy was homogenized, cold rolled, and then recrystallized to give about the same grain size. The details of these treatments are recorded in a previous publication.<sup>1</sup>

The tensile stress-strain curves for the alloys at elevated temperatures were obtained by means of equipment that has been described in the literature.<sup>1</sup> Strains were determined to a precision of better than  $\pm 0.001$  and the stresses were measured to an accuracy of about  $\pm 25$  psi. All tests, except where otherwise specified, were conducted at an average strain rate of about 0.118 per min.

Elevated temperatures were obtained by placing



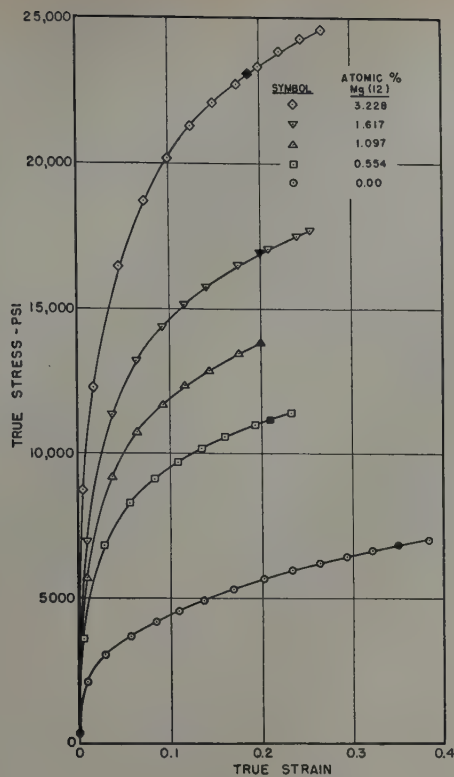


Fig. 5—Effect of magnesium on the work hardening of aluminum at 422°K.

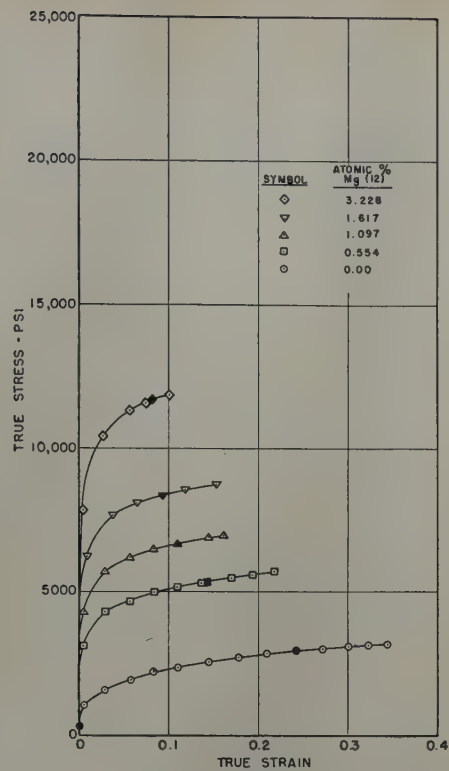


Fig. 6—Effect of magnesium on the work hardening of aluminum at 550°K.

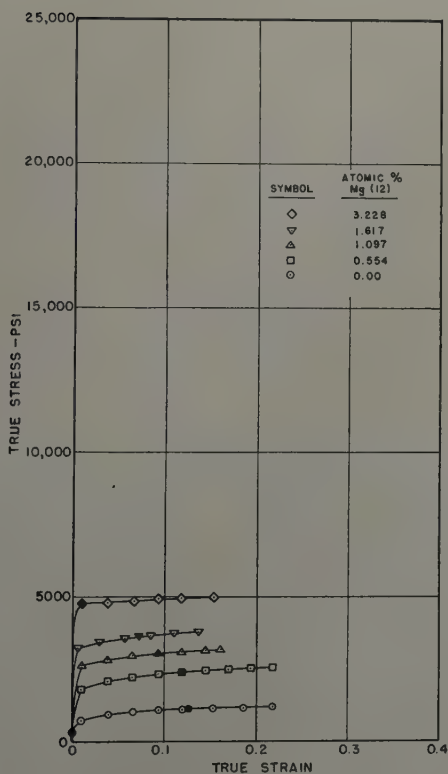


Fig. 7—Effect of magnesium on the work hardening of aluminum at 650°K.

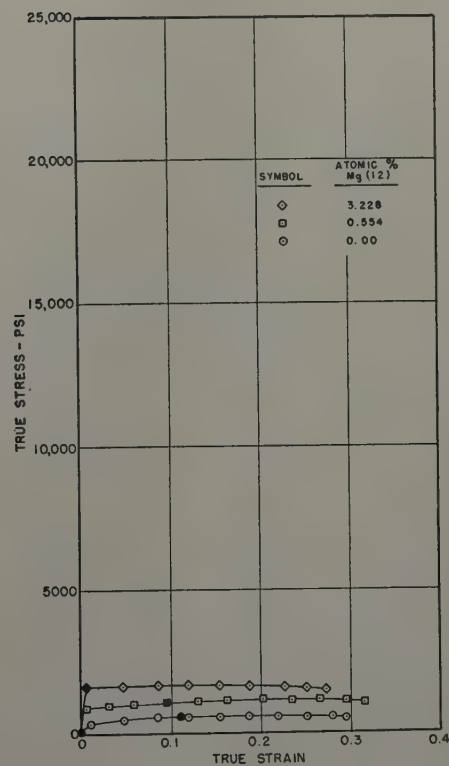


Fig. 8—Effect of magnesium on the work hardening of aluminum at 750°K.

a three element electric resistance furnace about the specimen. The upper, central, and lower zones of the furnace were each controlled independently by means of three commercial indicating controllers. A stainless steel liner 2½ in. in diam and 15 in. long was inserted in the center of the furnace in order

to further assure rather uniform temperature over the length of the specimen. Temperatures at three points along the 2-in. gage section of the specimen were measured during the test with iron constantan thermocouples bound to the specimen by means of flexible glass cord. Variations of temperature along

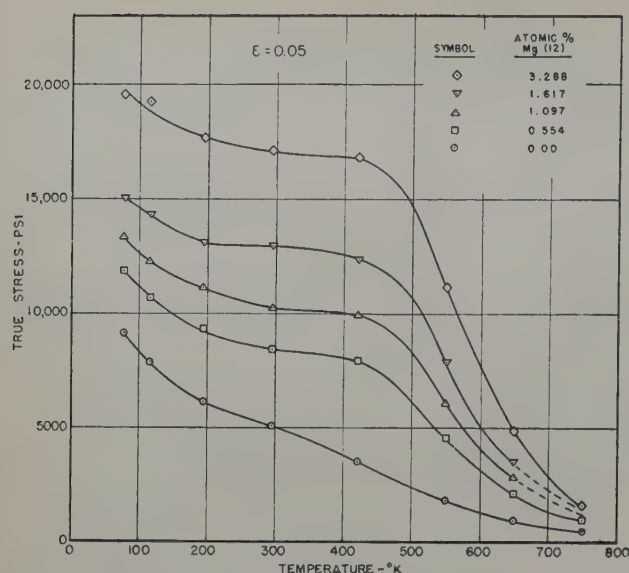


Fig. 9—Effect of test temperature on the flow stress of Al-Mg alloys for a true strain of 0.05.

the length of the specimen were held to less than  $\pm 1^\circ\text{C}$  during any one test.

### Experimental Results

The most pronounced effects of alloying additions on the elevated temperature tensile properties of  $\alpha$  solid solutions in aluminum were exhibited by the Al-Mg series of alloys. The true stress-true strain curves for these alloys over the range from  $78^\circ$  to  $750^\circ\text{K}$  are given in Figs. 1 to 8.

The point at which the maximum load was observed is shown by the solid symbol on each curve. At the lower temperatures of  $78^\circ$  to  $298^\circ\text{K}$ , specimens of all of the alloys began to develop a neck at this point. At the higher temperatures of  $422^\circ\text{K}$  and above, however, necking did not occur when the maximum load was reached. Consequently, the true stress-true strain curves at  $422^\circ\text{K}$  and above were obtainable beyond the point of maximum load.

The stress-strain curves given in Figs. 1 to 8 re-

veal that the effect of alloying additions on the plastic properties of  $\alpha$  solid solutions is dependent on the temperature of testing. At temperatures of about  $298^\circ\text{K}$  and below, magnesium additions result in appreciably higher stress-strain curves than those obtained for the pure aluminum. At the highest test temperature of  $750^\circ\text{K}$ , the alloying additions of magnesium had only a minor effect on the plastic properties of aluminum. The greatest effect of alloying is clearly seen to occur in the intermediate ranges of temperature from about  $298^\circ$  to about  $422^\circ\text{K}$  for the Al-Mg series of alloys. Similar trends also were observed for the remainder of the alloys that were investigated.

The temperature dependence of alloy strengthening upon additions of magnesium to aluminum is revealed more effectively in Fig. 9. In this diagram the flow stress at a fixed strain of  $\epsilon = 0.05$  is plotted as a function of the temperature for each magnesium alloy of the series, including pure aluminum. The strengthening of aluminum due to additions of

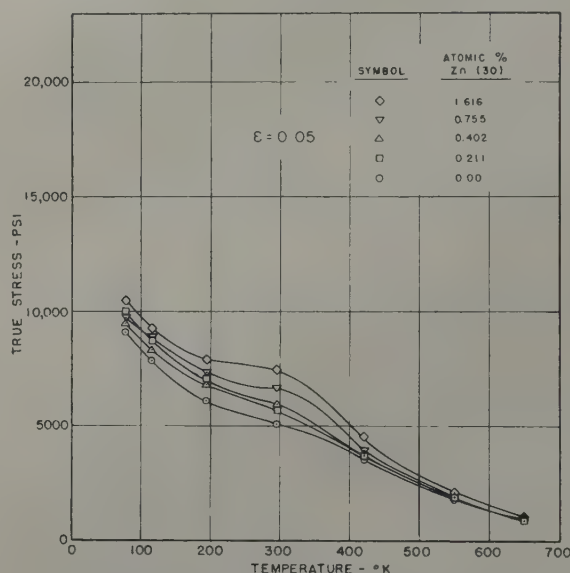


Fig. 11—Effect of test temperature on the flow stress of Al-Zn alloys for a true strain of 0.05.

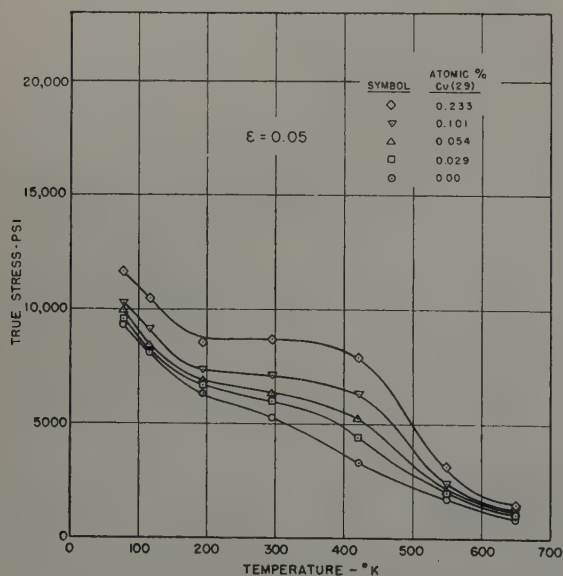


Fig. 10—Effect of test temperature on the flow stress of Al-Cu alloys for a true strain of 0.05.

magnesium is quite substantial over the range from  $78^\circ$  to  $298^\circ\text{K}$ . At  $700^\circ\text{K}$ , however, the strengthening due to magnesium additions is small and becomes negligible at about  $750^\circ\text{K}$ . The maximum effect of alloying additions on the strengthening of aluminum, however, occurs over an intermediate range of temperatures from about  $300^\circ\text{K}$  to about  $425^\circ\text{K}$ .

Similar data for the remainder of the alloys are given in Figs. 10 to 13. Although all of the alloys showed similar trends, the effects were much less pronounced than those of the magnesium series.

### Discussion of Results

The data reported under Experimental Results reveal that the strengthening of aluminum due to alloying additions is dependent on the test temperature. Apparently many factors contribute to this dependency and it will prove interesting to attempt to identify the most important ones.

Consider first the range of temperatures from that of liquid nitrogen ( $78^\circ\text{K}$ ) to that at which recovery first appears to have a significant effect on the tensile stress-strain curve (about  $300^\circ\text{K}$  for



pure aluminum.) In this range of temperatures the plastic properties of alloys are probably ascribable to two factors. The first consists of the increase in the initial flow stress due to alloying. This will be represented by  $\Delta\sigma_s$ , the solid solution strengthening, which is equal to  $(\sigma_{\text{alloy}} - \sigma_{\text{Al}})_{\epsilon=0}$ , the flow stress of the alloy minus that for pure aluminum, where both are measured at the same temperature and at infinitesimally small plastic strains. At greater strains, however, a second factor, namely the difference in strain hardening of the alloy and pure aluminum, enters the analysis. As shown in Figs. 1 to 4, alloying elements not only increase the initial flow stress but they also induce greater rates of strengthening with strain resulting in higher slopes of the stress-strain curves of the alloys than of pure aluminum when the curves are compared at the same temperature and strain. Thus at some given plastic strain larger than zero, the improvement in the plastic flow stress upon alloying  $(\sigma_{\text{alloy}} - \sigma_{\text{Al}})_{\epsilon}$  is due to the increase in the initial flow stress resulting from

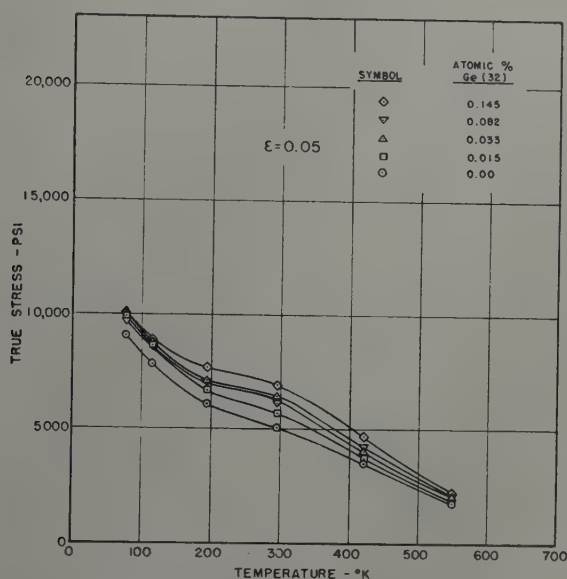


Fig. 12—Effect of test temperature on the flow stress of Al-Ge alloys for a true strain of 0.05.

solution strengthening  $\Delta\sigma_s$ , plus the increase in the flow stress of the alloy over and above the increase in the flow stress of pure aluminum upon strain hardening, namely  $\Delta\sigma_e$ .

A preliminary guess based on the hypothesis of dislocations can be made as to how  $\Delta\sigma_s$  varies with temperature. Solid solution strengthening is visualized as arising from the interaction forces between a dislocation and the solute atoms in the alloy. A major part of the interaction force is attributable to the internal stress fields surrounding the dislocation and the solute atoms. It also appears that part of the interaction force might have an electronic origin as revealed by the fact that solid solution hardening is dependent not only on the local lattice strains induced by the solute atoms but also on the difference in valence of the solute and solvent atoms.<sup>1</sup> Cottrell<sup>2,3</sup> has shown that the interaction force arising from the elastic strain energy interaction of a dislocation and a solute atom is proportional to the shear modulus of elasticity according to the relationship:

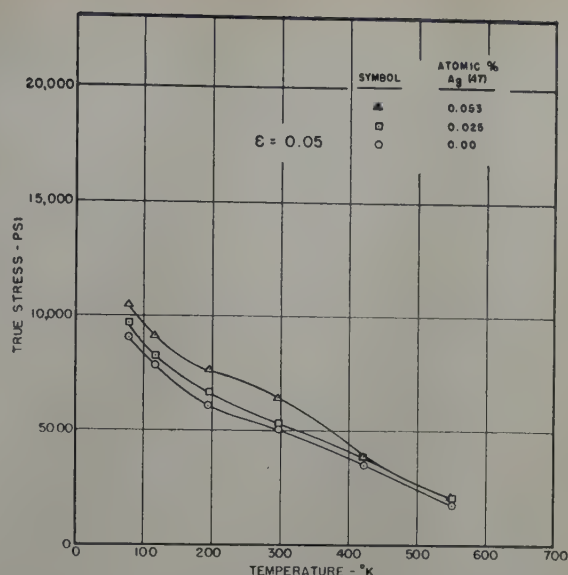


Fig. 13—Effect of test temperature on the flow stress of Al-Ag alloys for a true strain of 0.05.

$$F = \frac{4}{3} \frac{(1 + \nu)}{(1 - \nu)} \frac{G\epsilon r^3 \lambda}{R^2} \quad [1]$$

where,  $G$  is the shear modulus of elasticity;  $\nu$ , Poisson's ratio;  $r$ , the atomic radius of the solvent;  $\epsilon$  the local lattice strain due to the introduction of the solute atom;  $R$ , the distance between a solute atom and a dislocation; and  $\lambda$ , the strength of the dislocation (shear displacement when a unit dislocation traverses the crystal).

Cottrell's equation is admittedly an approximation to the facts, insofar as it is invalid for values of  $R$  approaching atomic dimensions and also because it is based on the interaction between a single solute atom and a single dislocation, whereas it is widely applied to solid solutions containing many atoms and dislocations. On the other hand, it probably gives a satisfactory qualitative, though distorted, picture of the facts.

In a pure metal  $R$  is infinite and  $F$  is zero. As alloying elements are added, however, the average value of  $R$  between the solute atoms and the dislocations decreases giving significant interaction forces  $F$ . If the alloy and the pure metal contain

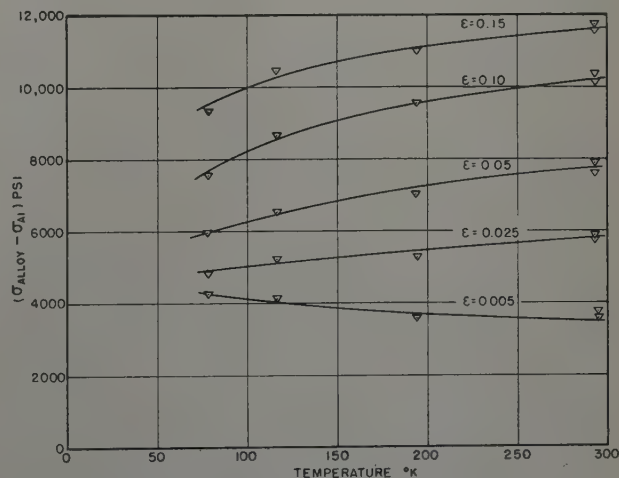


Fig. 14—Effect of strain and temperature on the increase in flow stress upon alloying aluminum with 1.618 atomic pct Mg.

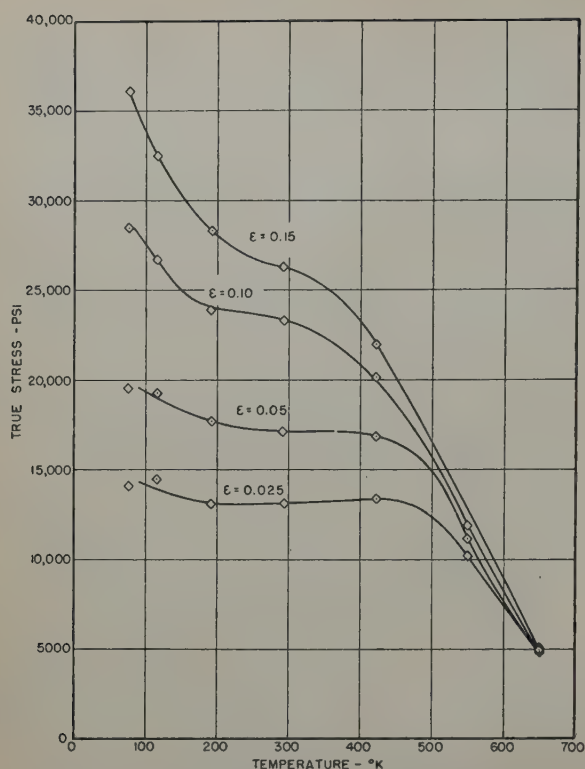


Fig. 15—Effect of test temperature on the flow stress of 3.2 pct Mg in aluminum alloy for various strains.

about the same density and distribution of dislocations, the increase in the initial flow stress upon alloying,  $\Delta\sigma_s$ , is primarily ascribable to the increase in  $F$  upon alloying. At higher test temperatures, however,  $F$  decreases because the shear modulus  $G$  decreases with increase in temperature. Consequently,  $\Delta\sigma_s$  should decrease with increasing temperature. This deduction is in part confirmed by the data shown in Fig. 14 for  $(\sigma_{\text{alloy}} - \sigma_{\text{Al}})_\epsilon$  at  $\epsilon = 0.005$ . At such small strains  $\Delta\sigma_s$  is small and, therefore,  $\Delta\sigma_s \approx (\sigma_{\text{alloy}} - \sigma_{\text{Al}})$ . The decrease in  $(\sigma_{\text{alloy}} - \sigma_{\text{Al}})_\epsilon$  for  $\epsilon = 0.005$  with increasing temperatures therefore suggests that  $\Delta\sigma_s$  decreases with increasing temperatures. Confirmation that  $\Delta\sigma_s$  is small at elevated temperatures is shown in Figs. 9 to 13. At the highest test temperatures where the alloys and pure aluminum recover extremely rapidly during the test, the flow strength of the alloys is not significantly greater than that for pure aluminum. These data strongly suggest that  $\alpha$  solid solution alloying is not particularly effective in improving the strength characteristics of a metal for application at temperatures well above the recovery temperature of the alloy. Other methods of strengthening, such as the introduction of intermediate phases, may prove more useful for strengthening in this range of temperatures.

The strain hardening of metals is commonly ascribed to the interaction forces between dislocations. Since alloying additions promote greater rates of strain hardening, it is consistent to assume that this is due to the more rapid accumulation of dislocations in the alloy than in the pure metal. The data of Figs. 1 to 8 reveal that the rate of strain hardening of aluminum and its  $\alpha$  solid solutions decreases with increasing temperatures, suggesting that the rate of accumulation of dislocations is less at the higher temperatures. The data of Fig. 14 show that  $(\sigma_{\text{alloy}} - \sigma_{\text{Al}}) = \Delta\sigma_s + \Delta\sigma_e$  increases for strains above

0.025 with increasing temperatures. Since  $\Delta\sigma_s$  decreases with increasing temperatures,  $\Delta\sigma_e$  must, therefore, increase with increasing temperatures. This suggests that the accumulation of dislocations upon straining decreases less rapidly with increase in temperature in the alloys than in pure aluminum. The detailed explanation of these observations is not yet clear to the authors. The practical significance of the observations, however, is obvious. Alloying additions primarily influence  $\Delta\sigma_s$  at low temperatures, whereas they primarily influence  $\Delta\sigma_e$  at high temperatures within the range where recovery is negligible. In fact, if an extrapolation of the data of Fig. 14 to  $0^\circ\text{K}$  be attempted, it appears as if the curves for various strains will coincide at about 4800 psi, suggesting that alloys of aluminum will strain harden no more rapidly than pure aluminum at the absolute zero temperature. At this temperature the flow stress of 1.62 atomic pct Mg alloy will exceed that for pure aluminum by about 4800 psi for all strains, whereas, at  $300^\circ\text{K}$  and a strain of 0.15, the flow stress for the same alloy will exceed that for pure aluminum by about 11,700 psi. Since the flow stress for aluminum decreases rapidly with an increase in temperature, these differences become yet more pronounced when they are based on a percentage basis.

Previous investigations have shown that pure aluminum begins to exhibit rapid recovery at just about  $300^\circ\text{K}$ . The data shown in Figs. 9 to 13 reveal that the stress-temperature curves of aluminum for a strain of 0.05 drops slightly in this range, indicative that recovery is occurring during the test. Presumably the rapid decrease in the flow stress with increasing temperature shown for the Al-Mg alloys in Fig. 9 at about  $425^\circ\text{K}$  is also indicative of rapid recovery during the test. Further evidence of this contention is revealed by the data recorded in Fig. 15, where it is noted that the temperature at which the flow stress first begins to decrease with increasing temperature is displaced to lower temperatures for the higher strains. Obviously for the strain rate employed in these tests, the 3.2 pct Mg alloy had recovered to the same flow stress for all recorded strains at about  $650^\circ\text{K}$ .

The remainder of the alloys also exhibit the same general trends of a rapid decrease in the flow stress

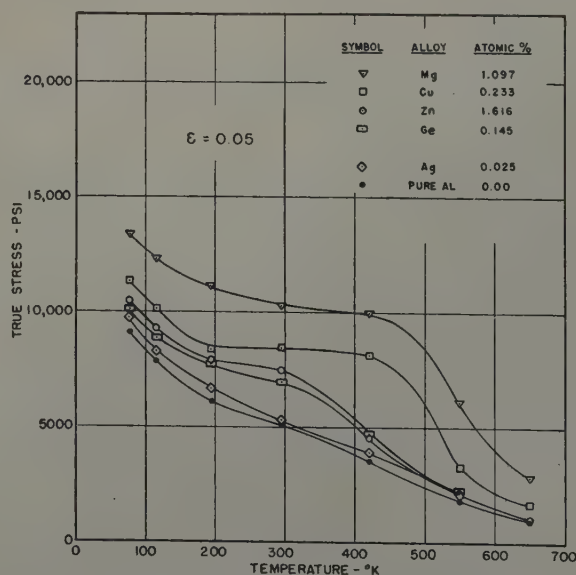


Fig. 16—Effect of test temperature on the flow stress of various aluminum alloys for a true strain of 0.05.



with increasing temperature in the recovery range of temperatures. The temperature at which the rapid decrease in flow stress first occurs appears to be practically independent of the concentration of the alloying elements in any one series of alloys as revealed in Figs. 9 to 13. On the other hand, as shown in Fig. 16, the temperature at which a rapid decrease in flow stress occurs with increasing temperature is sensitive to the particular alloying element that is present. In this respect the various alloying elements appear to have a unique effect on the plastic properties at elevated temperatures.

The effect of alloying elements on the plastic properties of aluminum alloys is particularly interesting over the intermediate range of temperatures from about 300° to 425°K. In this range the stress-temperature curves exhibit a plateau and, as shown in Fig. 15 for a strain of 0.025, in some instances actually reveal a hump. These data appear to suggest that the alloys are undergoing precipitation hardening over this intermediate range of temperatures in spite of the precautions exercised in selecting the compositions to be below the solubility limit at about 100°C as given by the best data currently available. Errors in extrapolation of the solubility data to atmospheric temperature could have been made, so that the highest composition of each alloy series might have exceeded the solubility limit. But it is quite inconceivable that the lowest compositions, which revealed identical trends, were also supersaturated. Nevertheless tests were made to ascertain whether precipitation had occurred. In view of the possible insensitivity of lattice parameter data and microscopic methods of detection, mechanical tests were considered to be more sensitive indexes of precipitation.

The planned test consisted of prestraining an alloy about 0.05 at 194°K, unloading, and then aging for 5 min at successively higher temperatures, following which the specimen was again to be mechanically tested at 194°K. It was anticipated that if precipitation were responsible for the observed plateaus in the stress-temperature diagrams of the alloys, the stress-strain curve at 194°K, following a prestrain and an aging treatment at some appropriate temperature, would lie above the stress-strain curve for the same alloy when the test had not been interrupted for aging.

The various stress-strain curves that were obtained on the 3.2 pct Mg alloy are recorded in Fig. 17. Curve A reveals that 5 min of aging at 194°K, following a prestrain at 194°K, had practically no effect on the stress-strain curve at 194°K. After aging for 5 min at 250°K, however, a distinct yield point was observed. This yield point became very pronounced following aging at about 295°K. But the yield-point effect was transient since after the yield phenomenon, the stress-strain curve of the aged material again coincided with that for unaged specimens at the same total strain. Thus, it was assumed that no real precipitation had occurred. After aging for 5 min at 371°K, however, the yield-point effect was reduced and the stress-strain curve after yielding fell below that for the unaged alloy, indicating that recovery had occurred during aging at this elevated temperature.

The absence of evidence for real precipitation and the introduction of a yield point upon appropriate aging suggested a strong parallelism between these data and that obtained upon the strain aging of steels.<sup>2,8,5</sup> It was, therefore, considered possible that

during aging the solute atoms might have migrated toward the dislocations under the interaction forces described by Cottrell, solutes larger than the solvent diffusing toward the expanded half of the dislocations and solutes smaller than the solvent diffusing toward the contracted regions of the dislocations. The interaction forces between the dislocations and the atmosphere of solute atoms which concentrated in its environs during aging would then be higher than in the homogeneous  $\alpha$  solid solution. Consequently, a higher than normal stress would be required to cause the dislocations to move after appropriate aging treatments. But once the dislocations have been displaced from their atmospheres, they again move in a more or less homogeneous dispersion of solute atoms and the flow stress again reduces to the usual value obtained for the unaged material at the same total strain.

One major difficulty with the above explanation of the strain-aging phenomenon centers about the small rates of diffusion of the solute atoms at the aging temperature. This will be discussed later. On the other hand, a Cottrell effect of this type could serve to explain the observed plateau in the stress-temperature diagrams even in the absence of precipitation. For example, at low temperatures the solute atoms cannot diffuse sufficiently rapidly to migrate with the dislocations. The increase in the flow stress of the alloy over that for the pure aluminum is then attributable primarily to the solution strengthening,  $\Delta\sigma_s$ , resulting from the interaction forces between the dislocations and the randomly dispersed solute atoms plus the effect of the increased rate of strain hardening  $\Delta\sigma_h$ , that occurs in the alloy. Although the second factor increases with

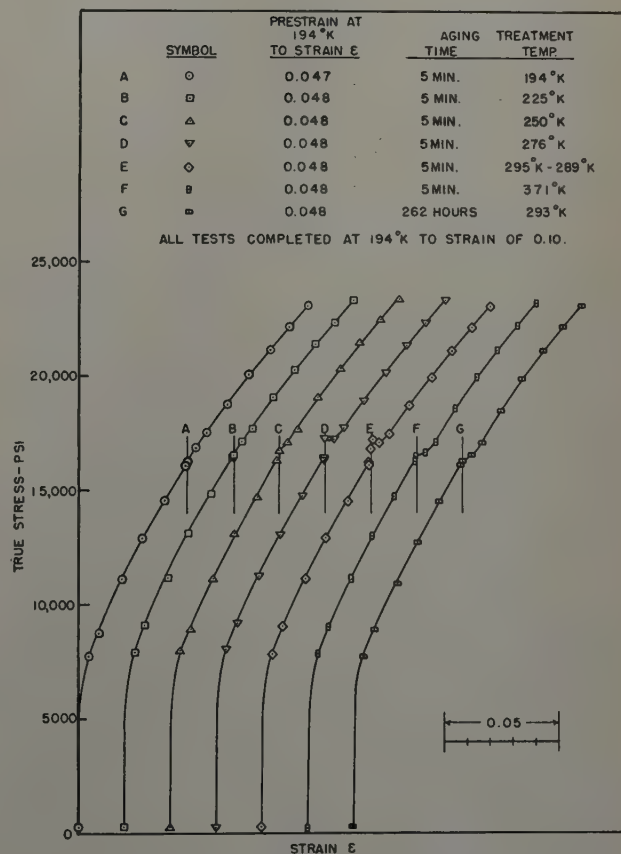


Fig. 17—Effect of strain-aging treatments on the true stress-true strain curve of 3.2 atomic pct Mg in aluminum alloy at 194°K.

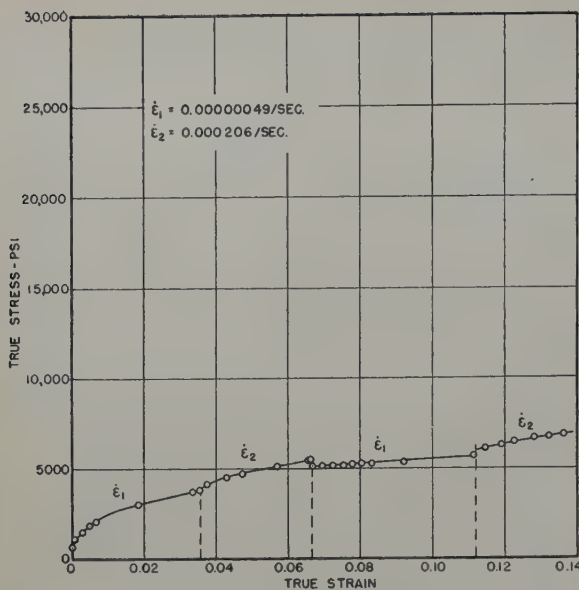


Fig. 18—Effect of strain rate on work hardening of pure aluminum at 295°K.

increasing temperatures, the first factor decreases with increasing temperatures. As higher test temperatures are used, the diffusivity of the solute atoms increases and finally reaches a value which permits their migration with the dislocation under the interaction forces that exist. When this occurs, the flow stress must be sufficiently great to continuously exceed the additional interaction forces between the dislocations and their atmospheres. Consequently, over some range of temperatures, the flow stress will decrease less rapidly than normal, leading to a plateau in the stress-temperature diagram which will be terminated at higher temperatures where rapid recovery occurs. Thus, the increase in the flow stress at high temperatures upon alloying is the increase in the flow stress due not only to the dislocations moving through a solid solution,  $\Delta\sigma_s + \Delta\sigma_e$ , but also to the increase in flow stress  $\Delta\sigma_e$  due to the fact that the solute atoms can migrate with the dislocation.

A critical experimental check on the above-outlined proposal for the cause of the plateau in the stress-temperature diagram is easily obtained. In general, an increase in strain rate causes an increase in the flow stress as shown in Fig. 18 for pure aluminum at 295°K. If the plateau that is obtained in the stress-temperature diagram is ascribable to a Cottrell effect, it follows that over the lower temperature range of the plateau, the atoms have just sufficient diffusivity to migrate with the dislocations. If either the temperature were reduced or the strain rate were increased, the solute atoms could no longer keep up with the moving dislocations. At a low strain rate at this critical temperature, for example, the solute atoms would migrate with the dislocations causing the increase in flow stress due to alloying to be  $\Delta\sigma_s + \Delta\sigma_e + \Delta\sigma_i$ , whereas at the higher strain rates the solute atoms could no longer diffuse with the dislocations, and, consequently, the increase in flow stress due to alloying would be only  $\Delta\sigma_s + \Delta\sigma_e + \Delta\sigma_e^*$ , where  $\Delta\sigma_e^*$  is the increase in the flow stress due to an increase in strain rate. Thus, an increase in strain rate, at some appropriate temperature, might result in a decrease in the flow stress, if  $\Delta\sigma_i$  is greater than the strain rate effect  $\Delta\sigma_e^*$ . Since this is contrary to the usual effect of

strain rate on the flow stress, it serves as a critical evaluation of the hypothesis. As shown in Fig. 19 the 3.2 atomic pct Mg alloy experiences a decrease in flow stress at 295°K with an increase in strain rate as predicted by a Cottrell effect. The large number of overlapping points on the fast strain rate curve are due to the fact that the load increased in a step-like manner for the given constant strain rate employed. Maximum and minimum load readings were observed and plotted in the figure. This occurrence is very similar to the process of deformation observed in aluminum alloys by McReynolds<sup>6</sup> and also Lubahn.<sup>7</sup>

Additional evidence that favors the hypothesis that the observed plateaus in the stress-temperature diagrams of the various aluminum alloys is attributable to a Cottrell effect might be obtained by calculating the density of the edge dislocations per square centimeter of the face of a unit cube of the alloy. If  $\rho$  is the density of the active edge-type dislocations per square centimeter of a unit cube of the alloy, the shear strain rate is:

$$\frac{\dot{\epsilon}}{2} = \lambda v \rho \quad [2]$$

where,  $\dot{\epsilon}$  is the tensile strain rate;  $v$ , the average velocity of the dislocations; and  $\lambda$ , the shear displacement per dislocation.

When the solute atoms diffuse just fast enough to keep up with the moving dislocations, the stream velocity of diffusion is just equal to the velocity  $v$  of the dislocations. It is possible, of course, that a Cottrell effect might also be noted when the velocity of streaming of the atoms is yet slightly below the mean velocity of the moving dislocations. This would give a slightly higher flow stress than in the complete absence of streaming, because many dislocations would carry the solute atoms with them over short distances. Thus, the critical velocity  $v$  of the motion of the dislocations for a Cottrell effect might be slightly larger than the streaming velocity of the solute atoms  $v'$  under the interaction energy between the solute atoms and the dislocations. Cottrell assumed that the streaming velocity  $v'$  is given by the Einstein equation:

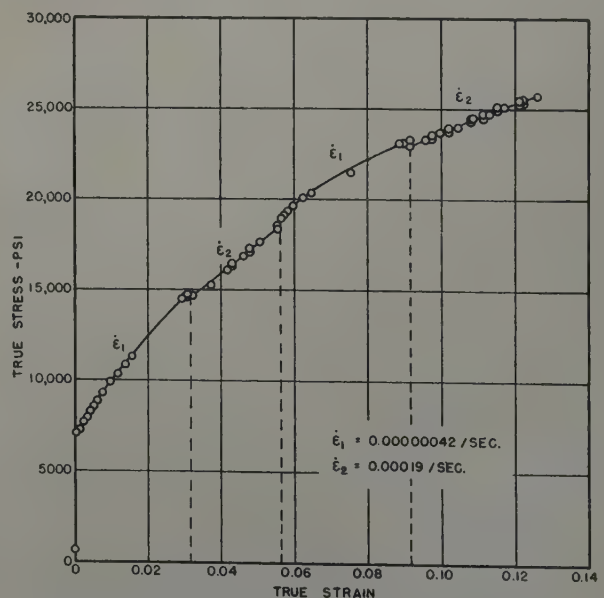


Fig. 19—Effect of strain rate on work hardening of 3.2 atomic pct Mg in aluminum alloy at 295°K.



$$v' = \frac{D}{kT} F \quad [3]$$

where,  $D$  is the diffusivity of the solute atoms;  $k$ , Boltzmann's constant;  $T$ , the absolute temperature; and  $F$ , the interaction energy between an atom and a dislocation (eq 1).

If  $v'$  approaches the order of magnitude of  $v$ , a Cottrell effect will be observed, and under these conditions:

$$\rho = \frac{\dot{\epsilon}}{2\lambda v'} = \frac{\dot{\epsilon} kT}{2\lambda D F} \quad [4]$$

The following data might be taken to estimate the value of  $F$  given in eq 1:

$$G = 2.65 \times 10^{11} \text{ dynes per sq cm}$$

$$\nu = 0.33$$

$$r = 1.43 \times 10^{-8} \text{ cm}$$

$$\lambda = 2.86 \times 10^{-8} \text{ cm}$$

$$\epsilon = 0.09$$

$$R = 5 \times 10^{-8} \text{ cm.}$$

The value of  $\epsilon$  was estimated from the change in lattice parameter from 4.0413Å to 4.0449Å upon the addition of 1 atomic pct Mg to aluminum. Then

$$\epsilon = \frac{100 \Delta a}{a} = \frac{0.0036 \times 100}{4.04} = 0.09. \text{ The value of } R$$

was estimated by assuming a random distribution of the magnesium atoms in the 3.2 atomic pct Mg alloy. Since there are 4 atoms per unit cell in aluminum the volume surrounding a magnesium atom would be  $\left(\frac{100}{p}\right) \frac{a^3}{4}$  where  $p$  is the atomic percentage of magnesium. The mean distance,  $R$ , between any dislocation and an atom is then given by:

$$4/3 \pi R^3 = \frac{100}{p} \frac{a^3}{4}$$

Introduction of 3.2 for  $p$  and  $4.04 \times 10^{-8}$  cm for  $a$  gives  $R = 5.0 \times 10^{-8}$  cm. Of course, the data reveal that the initiation of the plateau in the stress-temperature diagrams occurs at approximately the same temperature for all compositions, suggesting that this estimate is not critical. Introducing these values into eq 1 reveals that  $F \cong 10^{-6}$  dynes.

In order to estimate  $\rho$  from eq 4 the following data were assumed:

$$\dot{\epsilon} = \text{between } 0.4 \times 10^{-6} \text{ to } 190 \times 10^{-6} \text{ per sec} \\ (\text{from Fig. 19})$$

$$T = 295^\circ \text{K}$$

$$k = 1.38 \times 10^{-16} \text{ dyne-cm per degree}$$

$$\lambda = 2.86 \times 10^{-8} \text{ cm}$$

$$F \cong 10^{-6} \text{ dynes}$$

$$D = 5 \times 10^{-28} \text{ to } 5 \times 10^{-28} \text{ sq cm per sec.}$$

The values of  $D$  for magnesium were obtained by extrapolating from ordinary diffusivity data at elevated temperatures to atmospheric temperature. The wide range of values quoted above for  $D$  results from differences in the activation energies of magnesium in aluminum reported by various investigators.<sup>8-10</sup> It is conceivable that the correct value of  $D$  to be applied to the cold-worked Al-Mg alloy is several orders of magnitude greater than the extrapolated values. When the above values are introduced into eq 4 the values of  $\rho$  range from  $\rho_{\min} = 5 \times 10^{15}$  per sq cm to  $\rho_{\max} = 3 \times 10^{28}$  per sq cm. Obviously  $\rho_{\max}$  is much too large. On the other hand,  $\rho_{\min}$  begins to approach the value of  $\rho$  of  $10^{12}$  quoted

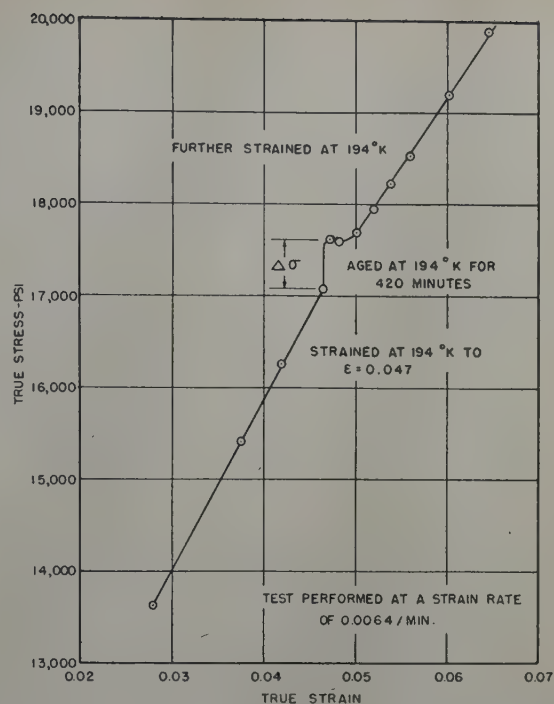


Fig. 20—Effect of a strain-aging treatment on the true stress-true strain curve of 3.2 atomic pct Mg in aluminum alloy at 194°K.

by Seitz and Read<sup>11</sup> for severely cold-worked metal. If the actual diffusivities in the cold-worked metal could be about 5000 times those for the annealed state,  $\rho_{\min}$  would reduce to about  $10^{12}$  in fair agreement with the estimate made by Seitz and Read. It appears, however, that several improvements in analysis and data will have to be made before quantitative agreement between theory and experiment can be achieved in this field.

Although the decrease in flow stress resulting from an increase in strain rate is probably ascribable to the fact that the solute atoms cannot diffuse sufficiently rapidly to migrate with the dislocations, it is by no means certain that the yield-point phenomenon upon aging is also attributable to the diffusion of the solute atoms to the dislocations. It is quite possible that the dislocations might migrate with greater ease toward the solute atoms during aging than the solute atoms can migrate toward the dislocations. If the solute atoms were diffusing toward the dislocations, the activation energy for the yield-point phenomenon would be that for the diffusion of the atoms, but if the dislocations were more mobile than the solute atoms the activation energy for the strain-aging process should be that for the activation of dislocations. Inasmuch as dislocations are activated during recovery at 298°K in pure aluminum, whereas the rate of migration of solute atoms is quite low at this temperature, preference must be expressed for the process involving the migration of dislocations to account for the observed yield-point phenomenon. This preference is emphasized by the data shown in Fig. 20. Careful prestraining at 194°K at a slow strain rate of  $\dot{\epsilon} = 0.0064$  per min, unloading, aging at 194°K for 420 min, and then continuing the straining at 194°K gives a well-defined yield point. At this temperature the diffusivity of magnesium in aluminum is about  $10^{-30}$  sq cm per sec, strongly suggesting that the yield point induced by strain aging cannot be ascribed to the migration of the solute atoms. The values of the yield-point hump  $\Delta\sigma$ , which is defined in Fig. 20,

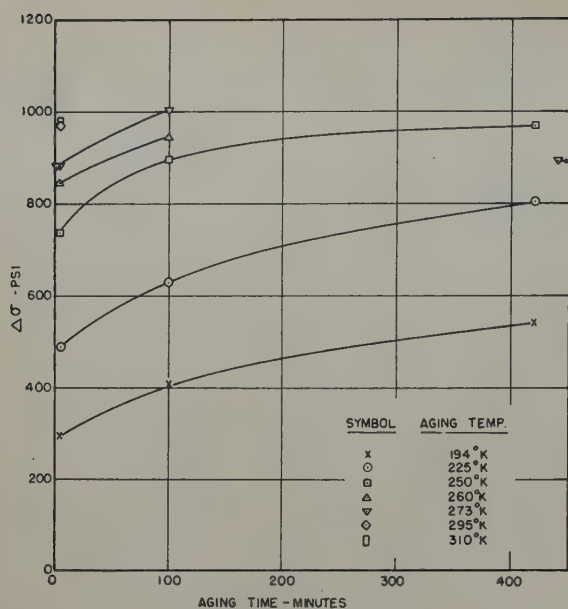


Fig. 21—Effect of strain-aging treatments at various times and temperatures on the increase in flow stress  $\Delta\sigma$ . 3.2 atomic pct Mg in aluminum alloy.

were obtained at 194°K after aging for various times and temperatures as shown in Fig. 21. Calculations based on these data suggest that the activation energy for the aging process is indeed low. No single activation energy, however, could be found. For small values of  $\Delta\sigma$  a low average activation energy of about 8000 cal per mol was obtained. The average activation energies for higher values of  $\Delta\sigma$  were estimated to be about 10,000 cal per mol, and yet higher values of  $\Delta\sigma$  suggested average activation energies of about 15,000 cal per mol. Since these values of the activation energy are less than half of the accepted values of activation energy for diffusion of magnesium in aluminum, the aging process cannot be attributed to diffusion of magnesium. These trends of increasing activation energies for increasing values of  $\Delta\sigma$  are highly reminiscent of the variation in activation energies for recovery which were previously reported.<sup>12,18</sup> It appears as if the smaller loops of the dislocations which have lower activation energies migrate rapidly and subsequently the more difficultly activated dislocation loops are induced to migrate to the solute atoms. Thus, the mean activation energy for the process steadily increases as the process proceeds.

### Conclusions

- 1—The effect of various alloying elements on the plastic properties of  $\alpha$  solid solutions of aluminum at elevated temperatures was studied.
- 2—The solid solution strengthening of the annealed metals decreases with increasing temperature as predicted by the dislocation theory.
- 3—On the other hand, the alloys exhibited greater relative rates of strain hardening than aluminum as the test temperature was increased.
- 4—Solid solution alloying is not very effective in improving the flow strength of aluminum at high temperatures where both the pure aluminum and the alloy recover rapidly.
- 5—In an intermediate range of temperatures from 300° to 425°K, the alloys showed the most pronounced improvement in flow stress over that for pure aluminum.
- 6—Some of this improvement was attributed to

the restraint offered by the alloying elements to recovery.

7—The major factor causing solid solution hardening in the intermediate range of temperatures, however, was shown to arise from the migration of the solute atoms with the dislocations as postulated by Cottrell.

8—When aluminum alloys are aged after straining, they develop a yield point. This occurs even when the straining and aging is done at 194°K and is probably attributable to the migration of dislocations to the solute atoms.

### Acknowledgments

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# Structural Studies of Plastic Deformation

## In Aluminum Single Crystals

by N. K. Chen and C. H. Mathewson

Single crystals of high purity aluminum of various orientations were carefully documented after plastic extension. Special attention was given to the formation of slip lines, deformation bands, and asterism. An explanation for the geometry and mechanism of formation of deformation bands is considered.

WHILE the general process of plastic extension of face-centered cubic metals is well understood,<sup>1</sup> the accompanying structural changes due to slip and rotation are far more complex than ordinarily assumed.<sup>2-5</sup> In the case of stretched single crystals of aluminum, the complicated behavior is especially marked by the formation of deformation bands, as first indicated by Collins and Mathewson.<sup>3</sup> Such bands were believed by them and also by others,<sup>6, 7</sup> who have discussed banded structure in general, to represent one of the important modes of lattice reorientation and to be intimately connected with the recrystallization process. Yet, despite their fundamental importance to the understanding of the mechanism of both plastic deformation and recrystallization, practically no study of the crystallographic features of these bands in their relationship to the conventional slip process has been attempted.

This paper describes part of an extensive investigation on the structural behavior during plastic deformation of aluminum single crystals and is especially concerned with the characteristics of deformation bands. The investigation of the subsequent recrystallization of deformed aluminum single crystals will be discussed in a later publication.

### Experimental Procedure

Single crystal specimens of 99.996+ pct pure aluminum, 1/2 in. in diam and 5 to 6 in. in length were made both by the Bridgman method<sup>8</sup> and by a modified temperature gradient method.<sup>9\*</sup>

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Crystals were selected in which the lineage deviation did not exceed 2°; i.e., as determined from the back-reflection Laue X-ray photograms. These crystals were radiographed to insure that no internal porosity was present. The orientations showed good coverage of the whole area of the Taylor and Elam triangle.<sup>1</sup> Orientations of the crystals were obtained by the back-reflection Laue technique described by Greninger.<sup>10</sup>

Crystals so selected were tapered very carefully in a lathe to obtain a linear decrease in diameter from 0.500 to 0.350 in. along a gage length of 3 in. This is considered desirable because it permits a strain gradient to be introduced in a single specimen at one initial orientation. The advantages of tapered crystals for studying the development of slip lines and recrystallized grains have been pointed out by previous investigators.<sup>11</sup> The cold-worked layer resulting from the machining operation was removed by alternate etching in aqua regia and careful polishing with 2/0 emery paper until undistorted Laue back-reflection spots were obtained. A homogenization treatment at 600°C for 24 hr was then introduced to insure the removal of residual stress. Two of the crystals so prepared were also checked by use of a glancing angle technique. Using a copper target, at 30 kv and 10 microamperes, a monochromatic beam was positioned at right angles to the axis of the crystal about which it rotated. The time of exposure was 24 hr. From these X-ray photograms, it was concluded that the present method of preparation of single crystals is satisfactory.

Following this procedure, the crystals were electrolytically polished in a 2:1 solution of methyl alcohol and concentrated nitric acid. Intermittent

\* A third method, a particular type of strain-anneal technique, developed in the present investigation, was also used for specimen preparation. It differs in a striking way from the ordinary strain-anneal procedure in that a tapered single crystal of one orientation can be transformed to another single crystal of a different orientation by first stretching it (not a critical amount) and then annealing it isothermally at a high temperature. The details will be discussed in a separate publication.

polishing periods of from 10 to 12 min at a current density of 10 amp per sq dm resulted in a high polish and smooth metallographic surface. Fine black lines then were painted on each specimen at  $\frac{1}{4}$ -in. intervals. These intervals were carefully measured in a Zeiss metallograph at a magnification of X77, yielding an accuracy of  $\pm 0.05$  mm.

The straining of the specimens was carried out for the most part on a Southwark Emery 20,000-lb hydraulic testing machine equipped with self-aligning grips and gimbals. The rate of loading was approximately 100 lb per min, and the load values could be estimated to 5 lb. In two cases (first extension of crystals A-2 and A-4) the loading equipment devised by Miller<sup>12</sup> and modified by Rosi<sup>13</sup> was used. In their equipment, uniform flow of sand produced loading at approximately 3 lb per min. The average of repeated measurements of the gage intervals painted on each crystal before and after extension gave a mean value of elongation for each gage section after extension as measured by an optical micrometer. A series of back-reflection Laue photograms per gage interval gave reorientation values in terms of  $\lambda$  and  $\chi$ , where  $\lambda$  is the angle between the specimen axis and the primary slip direction and  $\chi$  is the angle between the specimen axis and the primary slip plane. These values were used to calculate the elongation, resolved shear stress and shear, according to classical crystal mechanics.

The gross orientation changes of each tapered crystal are plotted in Fig. 1. During extension the stress axes of the crystal rotated, generally, toward the slip direction in the usual manner. In some cases when a symmetry position was reached, the lattice rotation did not obey the classical behavior; i.e., towards an equilibrium position at  $\langle 112 \rangle$ . In these cases, the stress axes continued to rotate toward the slip direction. This behavior has been generally observed in cylindrical and tapered  $\alpha$  brass single crystals.<sup>11, 14</sup> It should be noted, however, that both the measured and the observed values of reorientation of any tapered section of the crystal constituted an average representation of the lattice changes during deformation. It became clear that after asterism had

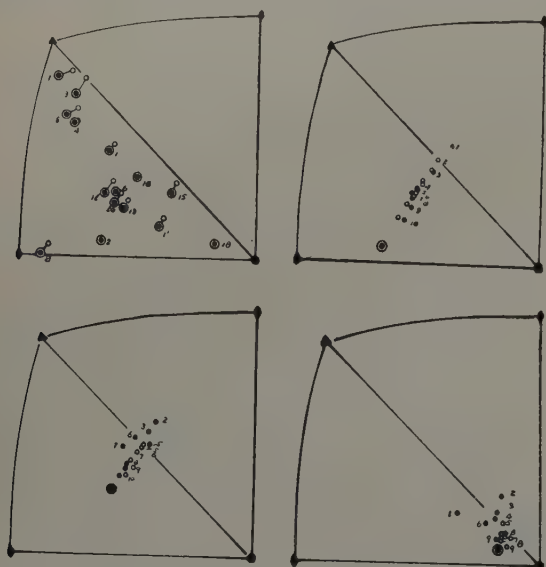


Fig. 1—Stereographic projection showing orientation of various aluminum crystals in relation to the axis of tension.  
 ○ — Original orientation (position of axis).  
 □ — Predicted orientation after deformation.  
 ● — Measured orientation after deformation.  
 a (upper left)—12 crystals with comparatively small deformation. b (upper right)—Crystal A-2. c (lower left)—Crystal A-6. d (lower right)—Crystal A-18.

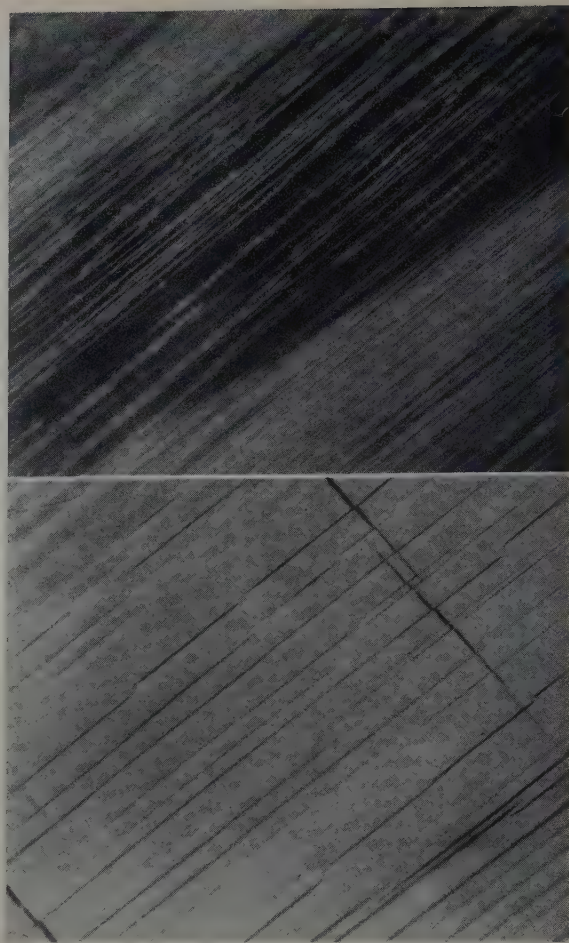


Fig. 2—Crystal A-18.

a (upper)—Pronounced cross slip at a position perpendicular to the plane containing the reference mark along the crystal and the stress axis. Shear is 0.16. Stress axis, horizontal; position No. 6 in Fig. 1d. Electrolytic polish. X150. b (lower)—Primary, conjugate, and cross-slip lines at a position perpendicular to the plane containing the reference mark along the crystal and the stress axis. The stress axis is horizontal. Shear is 0.24. X400.

developed, orientation determined by X-rays actually should be plotted as a range of orientation rather than a single axial position. The stress-strain curves indicated differences in the strain-hardening characteristics of the different specimens, but the nature and cause of these variations has not been established.

### Slip Lines and Deformation Bands

In all crystals, primary slip lines occurred in close association with cross-slip lines during the early stages of deformation. Early slip on the conjugate plane<sup>15</sup> was observed in crystals of certain orientations such as, A-7, A-5, A-16, and A-18. These lines were irregularly spaced (Fig. 2a) and, generally, discontinuous over primary slip clusters (Fig. 2b). It is clearly seen from Fig. 2b that the conjugate slip segments are displaced by primary slip lines formed subsequent to this slip on the conjugate plane.

Generally it is assumed that the slip bands in aluminum single crystals are quite regularly spaced. Nevertheless, in the present investigation, an orientational effect was found to exist. All crystals having their stress axes located near  $\langle 111 \rangle$  showed slip clusters during extension (Fig. 3a and b), whereas crystals oriented well away from  $\langle 111 \rangle$  exhibited dispersed slip lines (Fig. 3c, d, and e), or barely developed clusters; which were also observed in crystal A-18 having its axis near  $\langle 100 \rangle$  (see Fig. 2a). Since deformation bands were not found in crystals con-



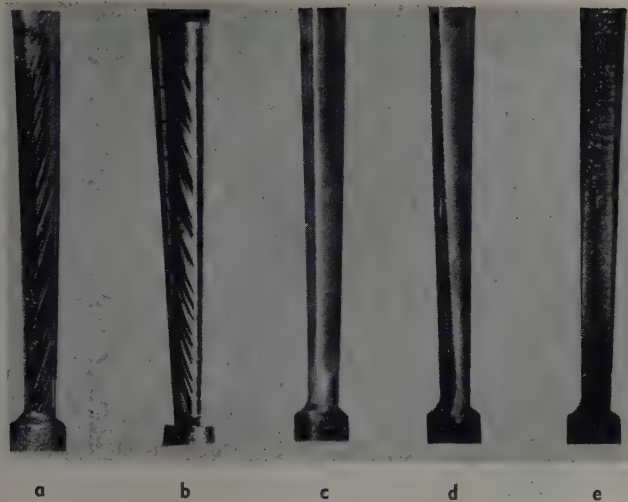


Fig. 3—Orientation effect on dispersion of slip lines.

a—Crystal A-7 showing slip clusters along the crystal; shear at small end of taper, 0.20, and at larger end, 0.09. b—Crystal A-3 showing same as a; shear is from 0.33 to 0.14. c—Crystal A-15, second extension; dispersed slip lines; shear is from 0.65 to 0.10. d—Crystal A-12', second extension; dispersed slip lines; shear is from 0.70 to 0.15. e—Crystal A-6, dispersed slip lines; shear is from 0.98 to 0.20. All photographs X1.

taining slip clusters, a close correlation seems to exist between the orientations concerned in the slip process and the generation of deformation bands. Furthermore, a similarity exists with brass crystals which always exhibit clustered slip lines, but no deformation bands as far as we can learn.

On an electrolytically polished surface, the deformation bands in an early stage of formation (shear about 0.05) can best be described as striations which reflect under very low magnifications or even to the naked eye. They would seem to disappear on observation under high magnification, as the observed slip lines give no indication of a banded arrangement. Thus, there is the likelihood of overlooking them in ordinary metallographic examination.

Deformation bands could be revealed by etching as shown in Fig. 4, with properly controlled conditions. A modified aqua regia solution (three parts HCl, one part HNO<sub>3</sub>, one part H<sub>2</sub>O) as an etchant after the crystal was polished with 2/0 emery paper was found to give very satisfactory and reproducible results. At the early stages of deformation (shear about 0.04 to 0.08), the boundaries of the bands could be easily identified as plane surfaces with elliptical peripheries on the cylindrical specimen. The distance between any two bands was not quite uniform, for at the large end of the tapered crystal they were more widely spaced than at the small end. Nevertheless, in the early stages of deformation, the average distance between bands was of the order of 1 mm.



Fig. 4—Deformation bands in crystal A-1'.

Shear is 0.11 to 0.08. Average distance between bands appearing on the surface is 1.2 mm. Etched in modified aqua regia solution. X4.

As the deformation increased, the bands also increased in intensity (but not in width) and became wavy. New bands of lesser intensity and more imperfect development were also generated between the older ones as shown in Fig. 5 representing crystal A-2. These pictures confirm the observation previously made by Collins and Mathewson<sup>3</sup> that the "... bands varied in thickness and character. When viewed from one point, they appeared straight and regular while from another, they appeared forked and wavy. When held in a certain position they reflected light strongly, as a twin would, while the remaining part of the crystal was dark."

On the unetched surface, the bands, after considerable extension seemed to show ridges and valleys as may be seen in Fig. 6a and b. With one of the crystals in which the strained surface was first etched and later repolished electrolytically, the bands appearing after the second extension could be resolved in some locations, indicating their narrow width, as shown in Figs. 7 and 8a. This width is about 0.038 mm and the average spacing about 0.3 mm. The slip lines crossing the band change their direction as would be the case if the material in the band lagged behind the material in the matrix during the process of lattice reorientation. This was found to be true by subsequent X-ray examination. In other cases revealing slip lines across a band of no clearly resolvable width, Fig. 8b, the directional changes of the slip lines were in agreement with the above statement.

#### Crystallographic Location of Deformation Bands

Two methods were used in determining the crystallographic location of deformation bands at the early stages of formation (shear below 0.10). One method consisted of measuring the azimuth angle of the band (the horizontal angle around the circumference of the crystal from the reference mark to the element containing the minimum or maximum point of the band) and the angle which the band made with the stress axis. The crystal was centered end for end on a one-circle goniometer, with the reference mark coinciding with the vertical cross-hair of a comparator which was also vertically located for the purpose of measuring the vertical difference from an arbitrary horizontal plane at various locations around the conical surface. With the diameter of the crystal corresponding to the maximum and minimum point of the band known, the required results could be obtained either graphically or by calculation. The other method was to determine the trace of the band on two known reference planes under the micro-



Fig. 5—Deformation bands of crystal A-2. a (left), b (right)—Second extension to a shear 1.03 at the small end and 0.20 at the large end. The wider bands make a smaller angle with the stress axis than the finer bands. Etched in modified aqua regia. X7.



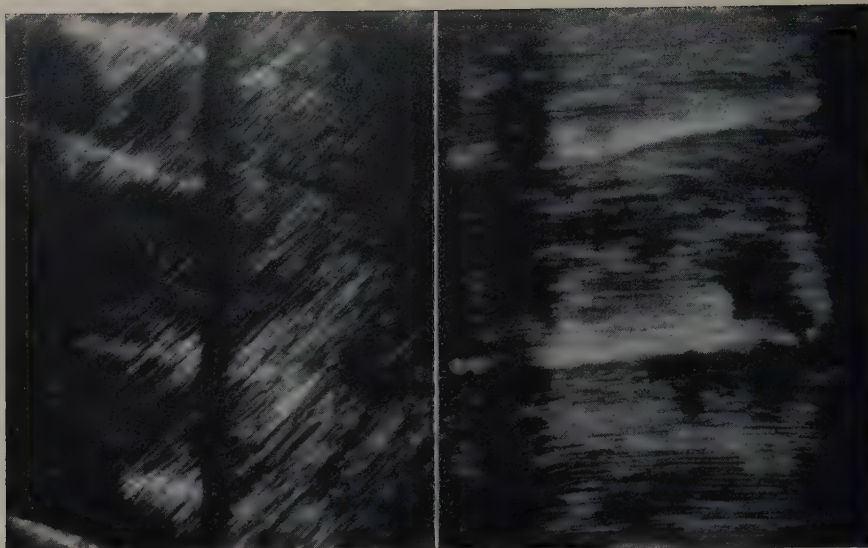


Fig. 6—Deformation bands in crystal A-12'. Second extension.

a (left)—Position shown is around the conical section between the major and minor axes of the glide ellipses. The stress axis is vertical as represented by the central scratch line. Shear, 0.3. Electrolytic polish. X60. b (right)—Position shown is perpendicular to the plane containing the major axis of the glide ellipse and the stress axis. Stress axis is vertical. Shear, 0.3. Electrolytic polish. X60.

scope. In all the cases the pole of the band was found to coincide with the slip direction within experimental error.

The resulting data are summarized in the stereographic plot, Fig. 9. It is seen that more than half of the crystals have produced bands but that an area of orientation spreading out from the octahedral pole is exempt from band formation. These crystals, without band formation, were characterized by irregularly spaced slip lines of a strongly clustered appearance. In the subsequent recrystallization studies, it was found that in the absence of band formation, the inner face of crystal growth lies parallel to the old glide plane, whereas with band formation, the growing face is decisively affected by the band.

#### Mechanism of Band Formation—X-ray Results

The fundamental process which causes the formation of deformation bands is believed to be due to the necessity for inhomogeneous rotations (within and adjacent to a band) in a forced pattern of flexural

gliding wherein the slip direction conventionally approaches the axis. This recalls the action of bend planes in zinc crystals, as described in 1934 by Miller.<sup>16</sup> However, in the present case, there are paired bend planes defining an intermediate band in which the process of reorientation is restrained,

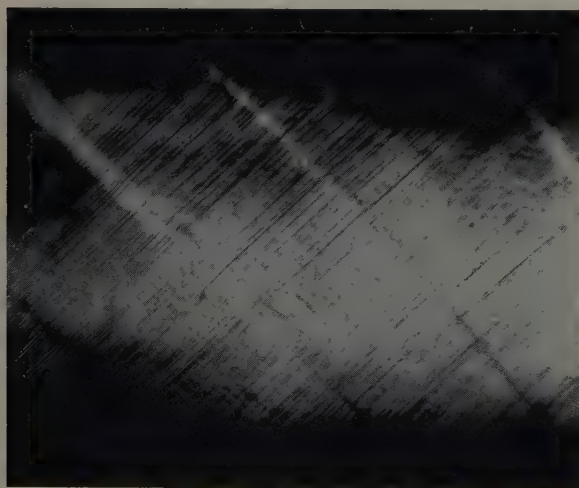


Fig. 7—Slip lines crossing deformation bands in crystal A-1'. Deformation bands were first generated after a shear of 0.05 corresponding to a reorientation of about 1°. Repolished electrolytically and again extended to a shear of about 0.20 corresponding to a reorientation of 8°. Taken at a position perpendicular to the plane containing the reference mark along the crystal and the stress axis. The stress is horizontal. X118.

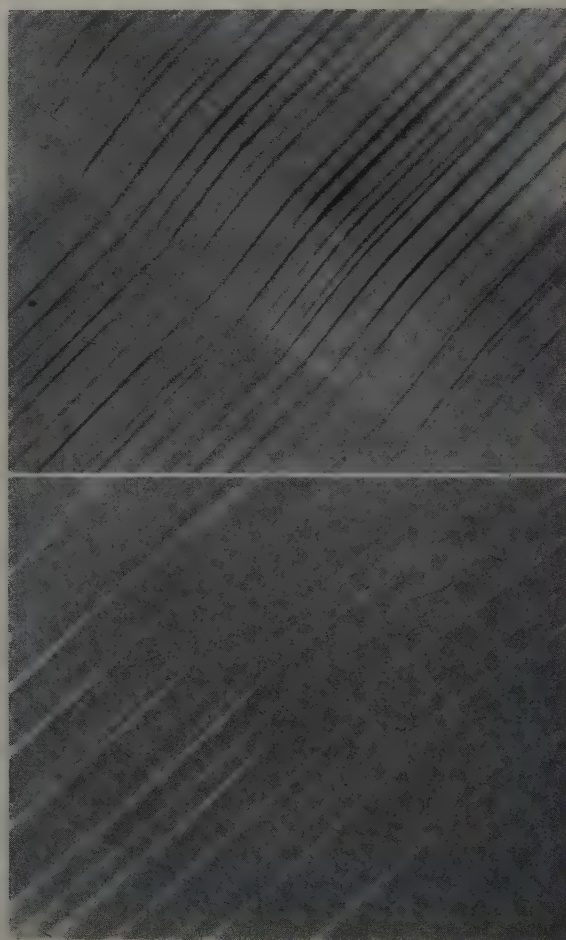


Fig. 8—Slip lines crossing deformation bands in crystal A-1'. a (upper)—Enlarged section of a deformation band shown in Fig. 7. X472. b (lower)—Same location as in Fig. 7. X1000.



or held to a minimum. This corresponds to that part of the Miller crystal which is prevented from slip and reorientation by an anchorage to polycrystalline material intentionally introduced for this purpose. X-ray studies of the bands in the very early stages of deformation (shear below 0.1) have indicated that both the axis of rotation and the sense of rotation corresponding to extension of the crystal could be properly correlated with the formation, structure, and location of the bands. An analysis of the situation follows:

As a rule, it was found that in the very earliest stage of deformation, when the bands are far apart (approximately 1 mm), the X-ray photograph taken on a band would give clear indication of distortion with a range of orientation of about  $2^\circ$ , whereas a photograph from the region between the two bands would show little or no asterism. This can be illustrated in Fig. 10a and b. In this case the width of the band was believed to be of the order of a few hundredths of a millimeter, and the spacing between bands along the crystal surface was about 1.7 mm. The X-ray beam was collimated by means of a pin-hole 0.5 mm in diam  $\times$  2.5 in. long. Therefore, when the X-ray beam was carefully adjusted to the band, it also covered some material outside of the band (Fig. 10a). But it impinged only on the slipped matrix when adjusted to the material between bands. After stereographically plotting the streaks seen in Fig. 10a, an axis of rotation could be located as clearly indicated in Fig. 11. This is the  $\langle 112 \rangle$  direction in the slip plane, normal to the slip direction. This axis of rotation could also be derived from plot of other X-ray photographs taken on the same band but with the beam located at a point around the conical surface  $90^\circ$  from the first position. It should be noted here that this axis of rotation is also the line of intersection of the primary slip plane and the plane of the deformation band.

In order to study the sense of the rotation, Fig. 10a and b and the film representing the original orientation of the crystal before extension were carefully superimposed. It was found, as indicated in Fig. 11, that the orientation of the slipped matrix corresponds to the left-hand part of each elongated streak, whereas the original orientation before ex-

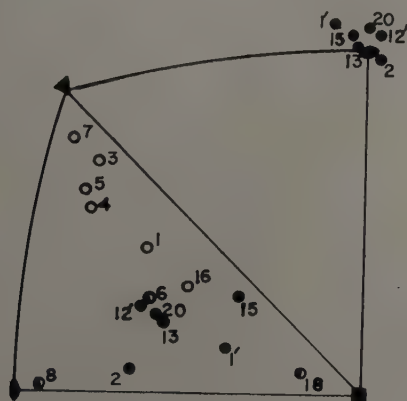


Fig. 9—Dependence of banding on initial orientation.

- — Initial orientations of crystals that subsequently formed deformation bands (the poles of the bands are shown clustering around the slip direction).
- — Initial orientations of crystals that did not form deformation bands.
- — Initial orientations of crystals that formed bands whose locations were not accurately determined.

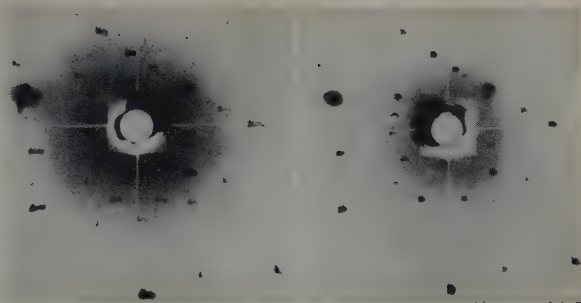


Fig. 10—Back-reflection Laue photographs taken on crystal A-12' after the first extension. Shear 0.08. X-ray beam was carefully located: a (left) on a deformation band, and b (right) between deformation bands immediately adjacent to position a.

tension coincides with the right-hand edge of the streak. This implies that while maxima in the Laue streaks represent the slipped matrix, the continuous background arises from the structure of the deformation bands. Examination of this situation shows that the sense of rotation about  $\langle 112 \rangle$  is counter-clockwise, which is in agreement with the rotational requirements of a slip process in which the slip direction, IV, approaches the stress axis, T, during extension. It should be noted, therefore, that the material in the band has lagged about  $2^\circ$  behind the matrix in this process of lattice reorientation. A standard projection summarizing these facts is shown in Fig. 12.

Similar analyses were carried out for rotations associated with deformation bands in other crystals. In all cases examined, excellent agreement with the above conclusions was obtained.

In crystals without band formation, no measurable amount of asterism could be noted in the Laue spots up to a shear of about 0.15. In such cases, X-ray photographs taken on and between areas with clustered slip bands represent the same orientation. This, again, brings out the similarity to brass crystals in which asterism is absent up to a shear of about 0.46.<sup>15</sup>

### Micrographic Analysis

The microstructure shown in Figs. 7 and 8a give good visual information concerning the formation and rotation of the bands. A stereographic projection referring to this particular region, representing the orientation changes of crystal A-1' after the second extension, is shown in Fig. 13. The axis of

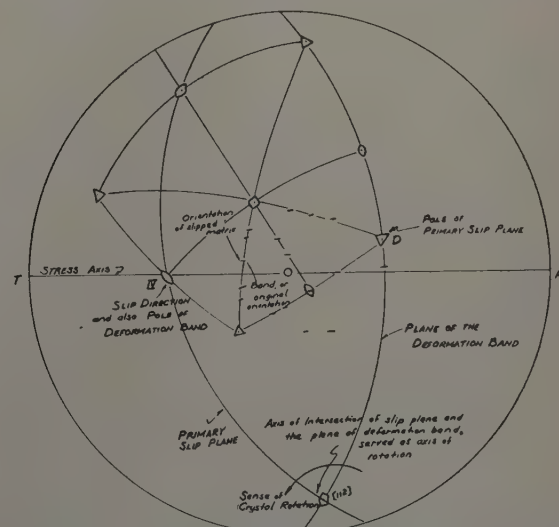
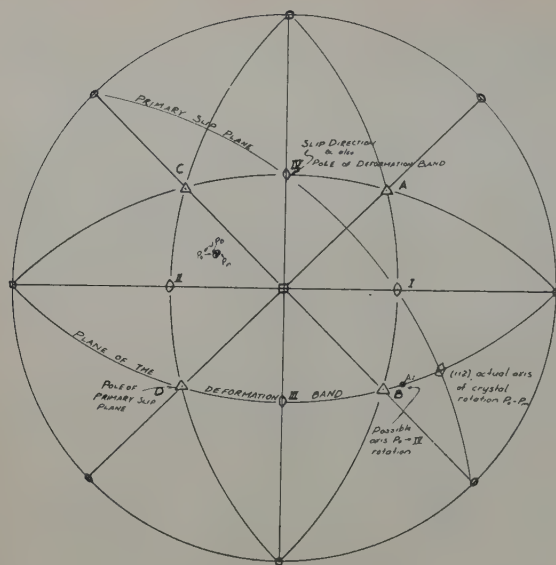
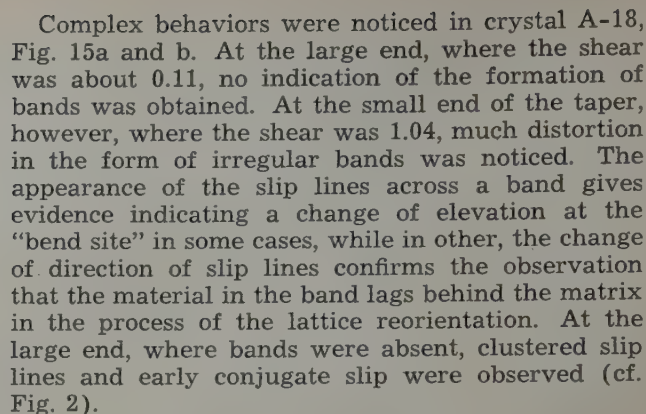


Fig. 11—Stereographic representation of the asterism of Fig. 10a.



rotation after the first extension; i. e., when the band was formed, was not measurable by means of X-rays (calculated shear, below 0.05), but the amount of axis rotation for the second extension was found to be  $8^\circ$ . Since the projection plane here coincides with the plane of observation, traces on the micrographs can easily be compared with the orientation plot. Thus, Fig. 14a and b were drawn from these indications. It is seen that the prediction embodied in Fig. 14b is in good agreement with the angular measurements actually made on the crystal, Fig. 14a, except that the axis of the band is not strictly parallel to *S-S* or *Q-Q*, following the analysis of Fig. 13, but lies in the direction *R-R* making a somewhat smaller angle with the stress axis. This probably indicates that the band was actually formed along the line *S-S*, as would be determined after the first extension, and has rotated toward the stress axis, but in the opposite direction to the rotation of the slip planes.



### Rotation of Deformation Bands

The question arises as to whether, after initial formation of a band, the two "bend planes" would move away from the stress axis during further rotation of the slip planes or would move toward the stress axis, but in the opposite direction to the rotation of the slip planes. Experiments seem to furnish many illustrations confirming this latter condition. It was more difficult to obtain clear evidence of the former condition, but it is believed that this also may have occurred.

For example, deformation bands developed in the first extension of crystal A-12' were carefully traced with a sharp pencil. The crystal was then subjected to a second extension causing both the bands and the markings to rotate. The bands, behaving quite similarly to the mechanical marks, rotated toward the stress axis as the crystal elongated. The coincidence of the marks and the boundaries was not quite perfect because the bands became wavy during the large amount of rotation. New bands formed between the earlier bands, with an even more wavy and irregular appearance, and a larger inclined angle to the stress axis than in the case of the initial bands. This implies that these new bands may have formed as a result of flexural gliding of the slip planes at their progressively reoriented positions.

Another example of the rotations of the bands themselves was encountered in the second extension of crystal A-2 plotted stereographically in Fig. 16 (cf. also Fig. 5). In the subsequent recrystallization process, new grains formed in this crystal along the boundaries of the initial bands but in their rotated positions.

No detailed study has been attempted with respect to the crystallite rotations within a narrow band.



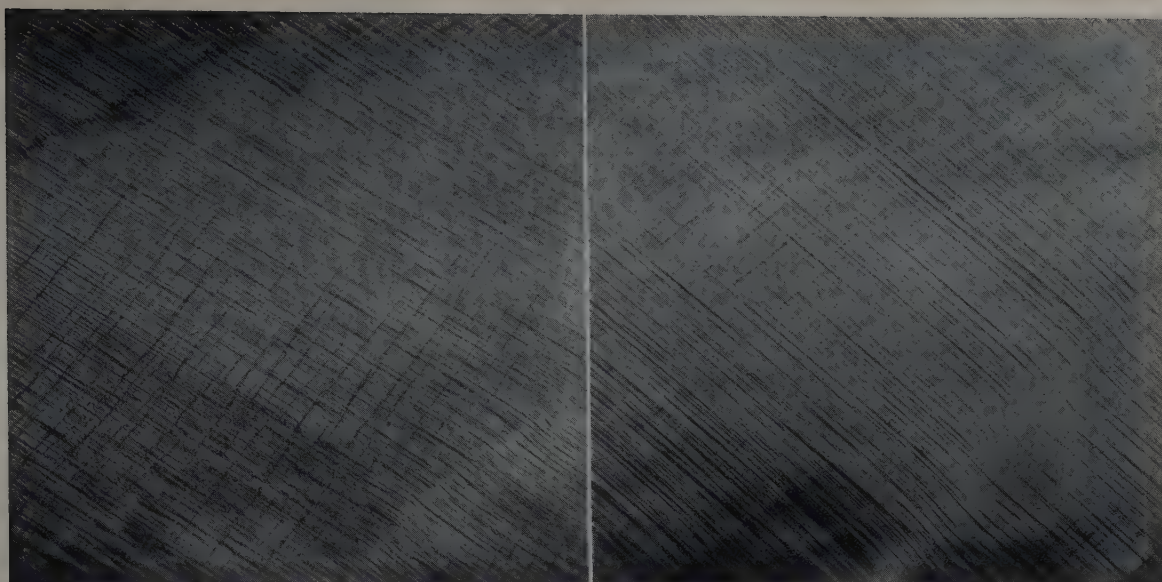


Fig. 15—Irrregular deformation bands in crystal A-18.

a (left)—Position shown is No. 1 of Fig. 1d in the plane containing the reference mark along the crystal and the stress axis. Shear is 1.04. Stress axis is horizontal. Electrolytic polish. X150. b (right)—Position shown is No. 4 of Fig. 1d in the plane containing the reference mark along the crystal and the stress axis. Shear is 0.30. Stress axis is horizontal. Electrolytic polish. X150.

which must accompany the progressive rotations of the matrix during deformation. X-ray photographs have indicated, however, that the range of orientation increased as deformation proceeded, confirming this type of rotation. The number of intensity maxima also increased. This may be due to the development of new bands.

## Discussion of Results

Deformation bands produced in the extension of aluminum single crystals possess, in general, the same characteristics as the banded structures found in other metals, after different types of deformation,<sup>6,7</sup> such as a gradual development of orientation differences between bands and matrix, and an unchanging width of the bands during progressive deformation. However, in the early stages of band formation, there is clear evidence of a process of crystal slip and abrupt flexural gliding at band boundaries, similar to the action of the "bend plane" which Miller observed in zinc.<sup>16</sup> A "bend plane" is the locus of the axes around which the slip planes

bend in this modification of simple flexural gliding. Thus, a pair of bend planes defines a band in which the reorientation lags behind that of the matrix material in the process of axial extension. A diagrammatic illustration is given in Fig. 17, embracing the following experimental facts:

- 1—The slip direction constitutes the pole of the band.
- 2—The reoriented material in the band lags behind that of the slipped matrix about  $2^\circ$  at an early stage of observation.
- 3—The axis of rotation in the process of band formation is  $\langle 112 \rangle$  which is also the intersection of the slip plane with the parallel planar boundaries of the band.
- 4—The slip lines change directions in crossing a band.

Recent studies by Hess and Barrett on the kink bands in zinc<sup>7</sup> also revealed an axis of rotation of the same general character. Thus, it would be profitable to examine other metals with respect to band formation and the details of reorientation during plastic deformation.

The tendency towards formation of deformation bands is orientationally dependent in the present case of axial extension of aluminum single crystals. Generally it has been assumed<sup>9</sup> that this tendency depends upon the orientation of the crystal or grain with respect to the direction of flow. Thus an iron

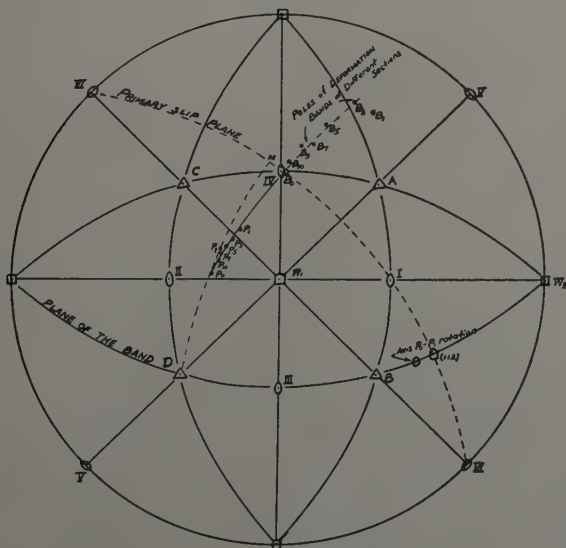


Fig. 16—Stereographic projection showing rotation of deformation bands in crystal A-2', second extension.

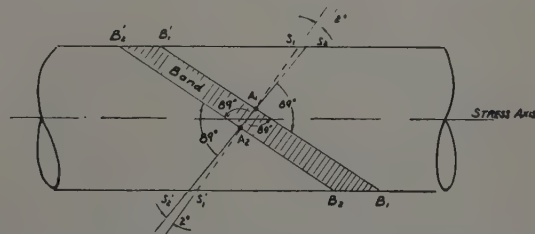


**Fig. 17—Hypothetical mechanism of formation of deformation bands. Plane of sketch contains stress axis and slip direction.**

$S_1A_1A_2S_1$  — Original position of slip plane.  
 $S_2A_1$ ;  $S_2A_2$  — Final position of slip plane.  
 $B_1A_1B_1$  — "Bend plane" 1.  
 $B_2A_2B_2$  — "Bend plane" 2.



crystal having a  $\langle 100 \rangle$  or  $\langle 111 \rangle$  axis parallel to the axis of compression will form no bands, but crystal of all other orientations become banded.<sup>6</sup>

Homogeneous rotation of the lattice during extension is prohibited because of constraints imposed by grips and by unslipped matrix material. The methods hitherto assumed by which a lattice could rotate and still satisfy the boundary conditions in aluminum have been flexural gliding<sup>17</sup> and crystal fragmentation.<sup>18</sup> The presence of asterism in the Laue X-ray photograms has been interpreted by various investigators as evidence in support of both mechanisms. In brass, collateral slip on cross and conjugate slip planes is assumed to contribute to lattice reorientation and thus modifies the pattern of asterism.<sup>4, 15</sup> It is shown here, however, that asterism in extended aluminum single crystals may arise entirely from the presence of deformation bands. In crystals which do not produce bands, no asterism was found up to a shear of 0.15, similar to the earlier observations on brass. Thus, it is believed that the absence of asterism in aluminum crystals indicates a modified condition of inhomogeneity due to cross-slip and early conjugate slip. Similar correlations between asterism and deformation bands in stretched aluminum crystals have recently been obtained by Cahn and Honeycombe.<sup>19, 20</sup>

There is a further similarity between aluminum single crystals oriented near  $\langle 111 \rangle$  and brass in that slip bands are much more irregularly spaced in such orientations, assuming a strongly clustered appearance. Thus the density of slip bands in such orientations should be expected to be much less than for crystals of other orientations. Actual measurement of slip bands in aluminum in the early stages of extension confirms this general orientational relationship.<sup>21</sup>

Strain hardening characteristics could not be correlated with differences in the appearance of slip lines. Since deformation bands were not found after extension in crystals of aluminum containing slip clusters nor in brass, it seems that dispersed slip lines indicate the probable generation of deformation bands. According to the mechanism previously described a band must traverse a slipped matrix throughout its entire course, and it is clear that prominent slip clusters are not conducive to band formation in the present sense.

### Conclusions

1—The tendency towards the formation of deformation bands in the plastic extension of aluminum single crystals is orientationally dependent. Axes oriented near  $\langle 111 \rangle$  in the standard projection do not lead to band formation.

2—The slip direction constitutes the pole of the band and the axis around which the slip direction changes its orientation is the intersection of the glide ellipse with the band ellipse, namely  $\langle 112 \rangle$ .

3—A mechanism is considered whereby a pair of bend planes defines a band in which the reorientation lags behind that of the matrix material in the process of axial extension.

4—Asterism found in the early stages of extension of aluminum is due to deformation bands, while the absence of asterism in crystals with no band formation in an early stage of deformation indicates that the inhomogeneities of deformation have been modified by cross-slip and early conjugate slip.

5—Crystals which develop bands reveal more regularly dispersed slip lines than crystals which do not

produce bands. In the latter case, a distinct clustering of the slip lines is invariably observed. This correlates properly with the plastic behavior of brass crystals, which develop slip clusters, but no deformation bands.

6—The band structure here observed possesses certain general features previously observed in deformation bands. A rotation of the bands after their initial stage of formation is confirmed and various possibilities in this direction are critically examined.

### Acknowledgments

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# Theory of Grain Boundary Migration Rates

by David Turnbull

IN isothermal recrystallization processes, new crystals generally grow into the matrix until they impinge upon other new crystals or an external surface, at constant linear rates  $G$ . Before impingement the perceptible course of growth can be described by the equation:

$$l = G(t - \tau) \quad [1]$$

where,

$$G = dl/dt,$$

$l$  is a crystal dimension measured in a constant direction,  $t$  is the time, and  $\tau$ , the nucleation period, is a positive intercept on the time axis. Fig. 1 is a schematic representation of  $l$  as a function of time for a recrystallizing grain.  $G$  is dependent upon temperature, driving energy (strain or surface energy), relative grain and boundary orientations, but is generally independent of time. The frequency of nucleation,  $\dot{N}$ , (time<sup>-1</sup> volume<sup>-1</sup>) can be defined by the equation:

$$\dot{N} = 1/\bar{\tau}V \quad [2]$$

where  $\bar{\tau}$  is the mean nucleation period and  $V$  is the volume of the specimen that has not recrystallized. The kinetics of primary and secondary recrystallization generally can be described satisfactorily in terms of the parameters  $\dot{N}$  and  $G$  only.<sup>1-3</sup>

After recrystallization is complete the average grain size  $\bar{l}$  increases with time by "normal grain growth;"  $d\bar{l}/dt$ , the average rate of grain growth, is strongly time dependent and has not yet been precisely related to  $G$  for the motion of the individual grain boundaries constituting the system.

It has been suggested<sup>4, 5</sup> that the elementary act in grain boundary migration is closely related to the elementary act in grain boundary self-diffusion. Although the distance of atom movement in the two processes may be somewhat different, there is reason to expect that the activated states may be very similar, so that the free energy of activation for grain boundary migration should be of the same order of magnitude as for grain boundary self-diffusion. Therefore, it is desirable to develop a satisfactory basis for comparing data on self-diffusion and grain boundary migration and to make such comparisons where possible.

## Theory

The formal theory of grain boundary migration rates is analogous to the theory for the rate of growth of crystals into supercooled liquids reviewed elsewhere.<sup>6-8</sup> Borelius<sup>9</sup> has shown that the latter theory describes, within the theoretical uncertainty, the growth of selenium crystals into supercooled liquid selenium. Mott<sup>9</sup> and more recently Smoluchowski<sup>10</sup> have derived expressions for the rate of

boundary migration in recrystallization. The treatment to be presented is similar to Mott's excepting that the formalism of the absolute reaction rate theory will be used.

The atomic mobility,  $M$ , in grain boundary migration is defined by:

$$G = -M\delta\mu/\delta x \quad [3]$$

where  $\mu$  is the chemical potential per atom and  $x$  is the coordinate measured in the direction of grain boundary movement. Let  $\Delta F$  be the free energy difference per gram atom on the two sides of the boundary and  $\lambda$  the thickness of the boundary. For  $RT \gg \Delta F$  the potential gradient across the boundary ( $\delta\mu/\delta x$ ) is essentially linear and it follows that:

$$\delta\mu/\delta x = -\Delta F/N\lambda \quad [4]$$

where  $N$  is Avogadro's number. According to the Nernst-Einstein equation,  $M$  is related to a diffusion coefficient,  $D_g$ , for matter transport in grain boundary migration by the equation:

$$M = D_g/kT \quad [5]$$

Substituting eqs 4 and 5 into eq 3 gives the basic relation between  $D_g$  and  $G$ :

$$G = D_g\Delta F/\lambda RT \quad [6]$$

$D_g$  values may be calculated from experimental values of  $G$  from eq 6 and directly compared with the coefficient of self-diffusion within the crystal,  $D_L$ , or the grain boundary self-diffusion coefficient  $D_B$ . However, a more convenient, though equivalent, basis for comparing atomic mobility in grain boundary migration and self-diffusion is through the constants of the absolute reaction rate theory. According to this theory diffusion coefficients may be written:<sup>11</sup>

$$D = \lambda^2(kT/h) \exp [-\Delta F_A/RT] \quad [7]$$

$\Delta F_A$ , the free energy of activation, is related to the measured energy of activation,  $Q$ , by the equation:

$$\Delta F_A = Q - T \Delta S_A - RT \quad [8]$$

where  $\Delta S_A$  is the entropy of activation. Substituting eqs 8 and 7 into eq 6 gives:

$$G = e \lambda (kT/h) (\Delta F/RT) \exp [(\Delta S_A)_g/R] \exp [-Q_g/RT] \quad [9]$$

where the subscript  $G$  refers to boundary migration. The relationship between the driving free energy and the free energy of activation in boundary migration is indicated schematically in Fig. 2.

Experience indicates that the variation of  $G$  with temperature can be described by:

$$G = G_0 \exp [-Q_g/RT] \quad [10]$$

where  $G_0$  and  $Q_g$  are generally temperature independent over wide ranges of temperature. Comparison of eq 9 with eq 10 gives:

$$G_0 = e \lambda (kT/h) (\Delta F/RT) \exp [(\Delta S_A)_g/R] \quad [11]$$

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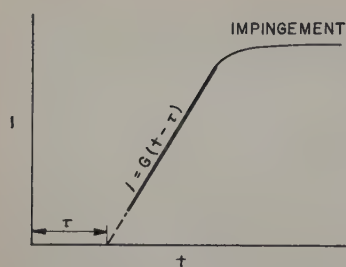


Fig. 1—Size of a growing grain as a function of time in primary or secondary recrystallization processes.

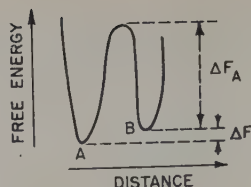


Fig. 2—Representation of free energy relationships between atoms on lattice sites A and B on opposite sides of a grain boundary.

Also it is found experimentally that:

$$D = D_0 \exp [-Q/RT] \quad [12]$$

By comparing eqs 7 and 12:

$$D_0 = e \lambda^2 (kT/h) \exp [\Delta S_A/R] \quad [13]$$

The relation between atomic mobility and free energy of activation is from eqs 5 and 7:

$$M = \lambda^2 (1/h) \exp [-\Delta F_A/RT] \quad [14]$$

From eq 14 it follows that the ratio of the atomic mobility in grain boundary migration to that in self-diffusion is, to within an order of magnitude, the same as the ratio of the corresponding factors  $\exp [-\Delta F_A/RT]$ .

#### Comparison of Free Energies of Activation for Self-Diffusion and Grain Boundary Migration

**Primary Recrystallization:** The free energy and entropy of activation in self-diffusion processes were calculated from the experimentally determined constants  $D_0$ ,  $Q_L$ , and  $Q_B$  (where  $L$  refers to lattice

self-diffusion and  $B$  to grain boundary self-diffusion) using eqs 13 and 8. However, in order to calculate the free energy  $(\Delta F_A)_G$  and entropy  $(\Delta S_A)_G$  of activation for boundary migration from the experimental constants  $G_0$  and  $Q_G$ , a value must be assigned to the "free energy"  $\Delta F$  driving primary recrystallization. It has been pointed out<sup>12</sup> that  $\Delta F$  cannot be evaluated by the methods of classical thermodynamics. However, it seems reasonable to assume that the driving energy for recrystallization is of the same order of magnitude as the energy stored in cold working,  $Z$ . According to the measurements of Taylor and Quinney<sup>13</sup> the maximum stored energy for metals  $Z_m$  is of the order of 25 to 50 cal per g atom and is usually reached at strains of 0.7 or more. For strains,  $\epsilon$ , of the order of magnitude ( $\sim 0.10$ ) of those for which  $G$  values in recrystallization are known, it may be assumed that  $Z = Z_m \epsilon/0.7$  and for most experimental conditions that are encountered in primary recrystallization:

$$Z_m \epsilon/0.7RT \sim \Delta F/RT \sim \epsilon \times 10^{-1.5 \pm 1}$$

It seems probable that  $\Delta F$  must be less than  $Z$  because of recovery prior to boundary migration. Due to the uncertainty in  $\Delta F/RT$  the calculated  $(\Delta F_A)_G$  may be in error by as much as  $\pm 2$  kcal per g atom.

In developing the theory it is assumed that the driving energy is uniformly distributed in the cold-worked matrix. More information about the state of the cold-worked matrix is needed to test this assumption. Bragg<sup>14</sup> and Heidenreich<sup>15</sup> have suggested that the cold-worked state of a crystal may consist of an aggregation of small misoriented blocks demarcated by intersecting slip planes. If it is further supposed that the strain energy is proportional to the surface area of these blocks, the theory of boundary migration driven by strain

Table I. Comparison of Energy, Entropy, and Free Energy of Activation in Self-Diffusion and Grain Boundary Migration

| Substance                                      | Strain | Grain Size, Cm | Temperature Range, °C | G <sub>0</sub> Cm per Sec | $\Delta S_A$ (Cal per Degree, Gram Atom) |                  |                  | $Q$ (Kcal per Gram Atom) |       |       | $\Delta F_A$ (Kcal per Gram Atom) |                  |                  |
|------------------------------------------------|--------|----------------|-----------------------|---------------------------|------------------------------------------|------------------|------------------|--------------------------|-------|-------|-----------------------------------|------------------|------------------|
|                                                |        |                |                       |                           | $(\Delta S_A)_L$                         | $(\Delta S_A)_G$ | $(\Delta S_A)_B$ | $Q_L$                    | $Q_G$ | $Q_B$ | $(\Delta F_A)_L$                  | $(\Delta F_A)_G$ | $(\Delta F_A)_B$ |
| a—Primary Recrystallization                    |        |                |                       |                           |                                          |                  |                  |                          |       |       |                                   |                  |                  |
| Aluminum <sup>17</sup>                         | 0.04   |                | 425-540               | 4.5x10 <sup>7</sup>       | 9.2                                      | 22.2             |                  | 37.5                     | 34.0  |       | 30.5                              | 17.2             |                  |
| Aluminum <sup>1</sup>                          | 0.051  |                | 310-370               | 1.5x10 <sup>10</sup>      |                                          | 60.7             |                  |                          | 59.0  |       | 32.0                              | 21.8             |                  |
| Rock salt <sup>20</sup>                        | ~0.1*  |                | 650-770               | 9x10 <sup>11</sup>        | 18.4 <sup>21</sup>                       | 40               |                  | 51.4 <sup>21</sup>       | 59.0  |       | 33.0                              | 19.8             |                  |
|                                                | ~0.3*  |                | 400-520               | 4.2x10 <sup>8</sup>       |                                          | 23               |                  |                          | 32.0  |       | 38.0                              | 15.0             |                  |
| Copper <sup>16</sup>                           | 0.10   |                | 300-320               | 10 <sup>13</sup>          | 14.22                                    | 45               |                  | 57.2 <sup>22</sup>       | 50.0  |       | 49.0                              | 23.8             |                  |
|                                                |        |                | 340-360               | 10 <sup>7</sup>           |                                          | 17.4             |                  |                          | 32.0  |       | 48.8                              | 21.1             |                  |
| Silicon ferrite <sup>19</sup>                  | 0.07   |                | 740-800               | 1.7x10 <sup>11</sup>      | 13.**                                    | 37.5             |                  | 59.7**                   | 73.0  |       | 46.2                              | 33.8             |                  |
| b—Secondary Recrystallization                  |        |                |                       |                           |                                          |                  |                  |                          |       |       |                                   |                  |                  |
| Copper <sup>2</sup>                            |        |                | 900-1000              | 10 <sup>11</sup>          | 14.                                      | 47               |                  | 57.2                     | 73.0  |       | 40.1                              | 15.5             |                  |
| Silver <sup>8</sup>                            |        |                | 433-533               | 2x10 <sup>8</sup>         | 9.24                                     | 11.8             | 220              | 46.0                     | 28.0  | 20.2  | 39.2                              | 19.1             | 18.7             |
| c—Normal Grain Growth                          |        |                |                       |                           |                                          |                  |                  |                          |       |       |                                   |                  |                  |
| Aluminum <sup>30</sup>                         | 0.03   |                | 400-500               | 10 <sup>21</sup>          | 9.2                                      | 93               |                  | 37.5                     | 87.0  |       | 30.8                              | 19.7             |                  |
| $\alpha$ brass <sup>31</sup><br>(comm. purity) | 0.03   |                | 450-700               | 10 <sup>9</sup>           |                                          | 38               |                  |                          | 60.0  |       |                                   | 27.8             |                  |
| $\alpha$ brass <sup>31</sup><br>(high purity)  | 0.03   |                | 450-850               | 10 <sup>4</sup>           |                                          | 15               |                  |                          | 40.0  |       |                                   | 26.0             |                  |

Superscripts except exponents of ten refer to references.

\* Given data on synthetic crystal expressed as stress. Strains estimated from stress-strain curve on natural crystals.

\*\* From data on self-diffusion on pure iron.<sup>23</sup>



energy is analogous to that driven by surface energy, where it is correct to suppose that  $\Delta F$  is uniformly distributed.

Data are available giving  $G$  as a function of temperature and strain in the primary recrystallization of some lightly deformed polycrystalline metals<sup>18-20, 1</sup> and more heavily deformed single crystals of rock salt.<sup>20</sup> The entropy  $(\Delta S_A)_G$  and free energy  $(\Delta F_A)_G$  of activation for grain boundary migration have been calculated from these data and are compared with the entropy  $(\Delta S_A)_L$  and free energy  $(\Delta F_A)_L$  of activation for lattice self-diffusion in Table Ia. In all cases  $\Delta F_A$  was calculated at the average temperature in the range of measurements.

Since no self-diffusion data for aluminum are available,  $Q_L$  was calculated from the empirical relation<sup>24</sup> discovered by Steigman, Shockley, and Nix<sup>22</sup> that  $Q_L \sim 0.7$  times the heat of sublimation.  $D_o$  was estimated from this value of  $Q_L$  using the Dushman-Langmuir equation.  $D_L$  for rock salt was calculated from the anion (slowest moving ion) conductivity data<sup>21</sup> using eq 5. The grain boundary thickness and diffusion distance  $\lambda$  were assumed to be  $2 \times 10^{-8}$  cm in all cases.

**Secondary Recrystallization:** Suppose that a large grain of dimension  $l$  grows into a recrystallized matrix having a small grain size  $l_o$ . Let the grain boundary free energy between matrix grains be  $\sigma$  and that between the large grain and the matrix be  $\sigma'$ . Then if the grain growth is driven by surface tension forces only  $\Delta F$  between the large grain and the matrix grains is given by:

$$\Delta F = KV (\sigma/l_o - \sigma'/l) \quad [14]$$

where  $K$  is a geometric factor of the order of unity and  $V$  is the gram-atomic volume of the material. When secondary recrystallization becomes perceptible  $l \gg l_o$ ,  $\sigma/l_o \gg \sigma'/l$  and eq 14 becomes:

$$\Delta F = KV\sigma/l_o \quad [15]$$

$G$  has been measured in the secondary recrystallization of copper<sup>2</sup> and silver.<sup>3</sup> The absolute grain boundary free energy in copper has been measured absolutely in several investigations.<sup>25-27</sup> The results have been summarized by Fisher and Dunn<sup>28</sup> who suggest 600 ergs per sq cm at 800°C as the best value for grains of large orientation difference. Assuming typical experimental conditions in the secondary recrystallization of copper to be  $l_o = 0.01$  cm and  $T = 1000^\circ\text{K}$  it follows:<sup>\*</sup>

$\Delta F/RT = K\sigma V/l_o RT \sim 10^{-5 \pm 1}$ . It can be assumed that  $\Delta F/RT$  in the secondary recrystallization of silver is also  $\sim 10^{-5 \pm 1}$ .  $(\Delta S_A)_G$  and  $(\Delta F_A)_G$  for secondary recrystallization calculated on the basis of these assumptions are compared with the corresponding constants for lattice and grain boundary self-diffusion in Table Ib.

**Normal Grain Growth:** Experimental data on normal grain growth are available from which  $d\bar{l}/dt$  may be calculated as a function of temperature and grain size. Thus far it has not been possible to deduce from this data the velocity of migration of particular boundaries driven by a known free energy. For the purposes of the present calculation it will be assumed that: 1— $d\bar{l}/dt = G$ ; and 2—

\* Because of the small orientation differences of neighboring grains  $\sigma < 600$  for cube texture copper. However, in view of the sharp increase in  $\sigma$  with increasing misorientation,  $\theta$ ,<sup>28</sup> an uncertainty no greater than a factor of 2 results from assuming  $\sigma \sim 600$ .

† The comparisons were not made for  $\alpha$  brass because of the uncertainty in the interpretation of the diffusion data.

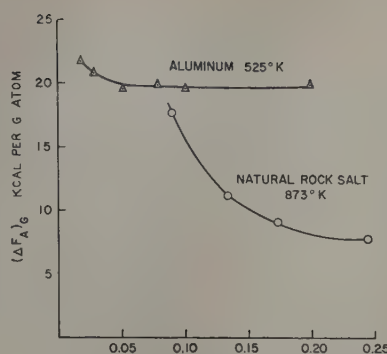


Fig. 3—Free energy of activation as a function of strain,  $\epsilon$ , in the primary recrystallization of polycrystalline aluminum<sup>1</sup> and rock salt single crystals.<sup>20</sup>

$\Delta F = K\sigma V/\bar{l}$  in normal grain growth.  $(\Delta F_A)_G$  calculated with these assumptions will be too large, possibly by 2 to 4 kcal per g atom. However, it will be seen that this uncertainty in  $(\Delta F_A)_G$  does not affect the validity of the general conclusion drawn from the calculations. The values of the entropy and free energy of activation in normal grain growth are summarized in Table Ic.

**Interpretation of the Results:** The most important conclusion that follows from the comparisons made in Table I is that the free energy of activation for self-diffusion within a crystal exceeds the free energy of activation in boundary migration by a large amount (10 to 25 kcal per g atom) that is much greater than the uncertainties in the calculation in all cases.† From this result it follows that the atomic mobility in grain boundary migration,  $M_G$ , is always larger by many orders of magnitude than the atomic mobility in lattice self-diffusion  $M_L$ ; e.g., in the secondary recrystallization of OFHC copper at 950°C,  $M_G = 10^8$  compared to  $M_L = 10^{3.8}$ .

There is good reason to expect that the grain boundary regions in metals are highly disordered relative to regions within the body of the crystal. Since it is further supposed that diffusion is promoted by crystal imperfections, it is not surprising that  $M_G \gg M_L$ . However, this result is not obvious from comparing  $Q_L$  with  $Q_G$  for  $Q_L$  is sometimes smaller, about the same, or larger than  $Q_G$ .

Data on the rate of self-diffusion at grain boundaries are available only for silver,<sup>29</sup> and it may be very significant that the free energy of activation  $(\Delta F_A)_B$  agrees closely with the free energy of activation  $(\Delta F_A)_G$  in the secondary recrystallization of silver. This fact suggests the possibility that the generalization  $(\Delta F_A)_B = (\Delta F_A)_G$  holds for grain boundary migration processes driven by interfacial tension. The results also suggest that the generalization  $(\Delta F_A)_B \cong (\Delta F_A)_G$  holds for primary recrystallization.

$(\Delta F_A)_G$  at 625°K as a function of strain has been calculated for Anderson and Mehl's<sup>1</sup> data on the primary recrystallization of aluminum and plotted in Fig. 3. For  $0.2 > \epsilon > 0.05$ ,  $(\Delta F_A)_G$  is independent of  $\epsilon$ . However, between  $\epsilon = 0.02$  and  $0.05$   $(\Delta F_A)_G$  decreases about 2 kcal per g atom, a number that is about 1000 times larger than the stored energy of cold working,  $Z$ . Also shown in Fig. 3 is  $(\Delta F_A)_G$  vs.  $\epsilon$  calculated from Muller's data<sup>20</sup> on the primary recrystallization of rock salt crystals at 600°C. It is evident that  $(\Delta F_A)_G$  is much more strain-sensitive for rock salt single crystals than for polycrystalline aluminum.

It might be inferred from inspection of the constants  $Q_G$  and  $(\Delta S_A)_G$  that the  $G$  values in the three investigations on aluminum are in wide disagreement. Actually  $(\Delta F_A)_G$  values for the temperatures

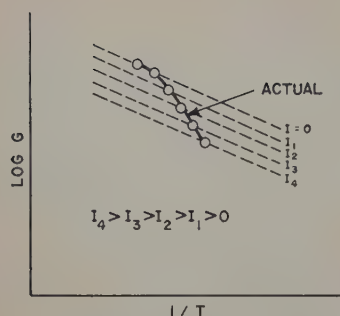


Fig. 4—Representation of  $\log G$  vs.  $1/T$  for various degrees of dispersion ( $I$ ) of inclusions at grain boundaries.

at which the measurements nearly overlap approximately agree. At  $400^\circ\text{C}$  for  $\epsilon = 0.05$ , Anderson-Mehl's<sup>1</sup> results give  $(\Delta F_A)_G = 18.0$  compared to 19.0 kcal per g atom obtained by Kornfeld-Pavlov<sup>17</sup> for  $\epsilon = 0.04$ . These values are in reasonable agreement with  $(\Delta F_A)_G = 24.5$  kcal per g atom for normal grain growth in aluminum at  $400^\circ\text{C}$ <sup>30</sup> in view of the fact that the theory as now formulated gives too large a value to  $(\Delta F_A)_G$  in normal grain growth.

Though the atomic mobility in grain boundary migration is many times larger than in lattice self-diffusion, the activation energy for the former process is often as great and sometimes even greater than for the latter process. These relations are consistent with the fact that the entropy of activation in boundary migration is generally 10 to 30 entropy units larger than in lattice self-diffusion. On the basis of the arguments used to account for  $(\Delta F_A)_L > (\Delta F_A)_G$ , it would be expected that  $Q_L > Q_G$ . Also there is no obvious reason for the entropies of activation for the two processes to be very different.

In order to account for these seeming anomalies Mott<sup>9</sup> has proposed the hypothesis that activation for grain boundary migration consists in melting several ( $n$ ) atoms at the boundary. According to this view the energy of activation for boundary migration is the energy necessary to fuse  $n$  atoms:

$$Q_G = nQ_f \quad [16]$$

where  $Q_f$  is the gram-atomic heat of fusion and may therefore bear no simple relation to  $Q_L$  (or  $Q_B$ ). On this picture the entropy of activation is the entropy gain in melting  $n$  atoms:

$$(\Delta S_A)_G = n\Delta S_f \quad [17]$$

where  $\Delta S_f$  is the entropy of fusion.<sup>‡</sup>  $n$  may be a function of strain, temperature and relative grain and boundary orientations. Mott's theory reduces the number of disposable parameters from  $(\Delta S_A)_G$  and  $Q_G$  to  $n$  only and can be tested by comparing  $(\Delta S_A)_G$  with  $n(\Delta S_f)$  where  $n$  is calculated from  $Q_G$  using eq 16. Mott showed that the theory accounts for the entropy of activation calculated from Anderson's and Mehl's data on aluminum and Smoluchowski<sup>30</sup> has shown that the theory accounts for the grain growth data of Beck, Holzworth, and Hu<sup>30</sup> on pure aluminum and of Burke<sup>31</sup> on  $\alpha$  brass of commercial purity.

In order to make a comparison of  $n\Delta S_f$  and  $(\Delta S_A)_G$  strictly in conformity with Mott's theory, it is necessary to modify the calculation of  $(\Delta S_A)_G$  by substituting  $n\Delta F$  for  $\Delta F$  in eq 11, since  $n$  atoms are transported in the elementary process. The values of the entropy of activation for boundary migration  $(\Delta S_A)_G'$  so calculated from all the available data are compared with  $n\Delta S_f$  and  $(\Delta S_A)_L$  in Table II.

Though  $(\Delta S_A)_G'$  and  $n\Delta S_f$  diverge widely in a few

<sup>‡</sup> Mott's formulation has been altered somewhat in order to make it conform to the absolute rate theory.

instances the comparisons in Table II indicate that Mott's theory in general successfully accounts for the unexpectedly large values of  $(\Delta S_A)_G'$ . In addition to the divergences noted the main objection to the theory as it now stands is the arbitrariness of the  $n$  values. Also in view of the small values of  $n$  ( $< 35$ ) it is not correct to ignore surface energy considerations in calculating the free energy of melting. On an energetic basis  $n$  should be unity if the surface energy is neglected.

One of the basic assumptions of the theory developed is that the driving energy does not change with temperature. An alternative theory for the large magnitude of the calculated  $(\Delta S_A)_G$  values is that they are more apparent than real due to a marked dependence of  $\Delta F$  upon temperature.  $\Delta F$  might change markedly with temperature due to matrix processes of recovery, grain growth, or solution of boundary retarding inclusions concurrent with boundary migration. Among these processes only the solution of inclusions is likely to lead to apparent values of  $(\Delta S_A)_G$  that are much greater than the actual values.

Following Zener<sup>32</sup>  $\Delta F$  for boundary migration retarded by inclusions may be expressed as:

$$\Delta F = (\Delta F' - K\sigma\rho V/\gamma_o) = \Delta F' - I \quad [18]$$

where  $\Delta F'$  is the driving free energy in the absence of inclusions,  $\rho$  is the volume fraction of inclusions in the matrix, and  $\gamma_o$  is the radius of the inclusion. In general  $I$  is likely to be a function that decreases with increasing time or temperature. However, suppose that at constant temperature  $I$  reaches a constant value in a time that is short relative to the period of boundary migration. Then with respect to boundary migration,  $I$  is a function of temperature only and  $G$  is independent of time. In Fig. 4  $\log G$  is represented schematically as a function of  $1/T$  for various constant values of  $I$ , each characteristic of a different temperature. This family of curves all have the same value of  $Q_G$ , but apparently different values of  $(\Delta S_A)_G$  that may be quite small. However, since  $I = f(T)$  the observed relation for  $\log G = f(1/T)$  will be schematically as shown by the solid curve through the circles and the apparent values of  $Q_G$  and  $(\Delta S_A)_G$  will be much larger than those characteristic of  $I = 0$ .

The inclusion hypothesis predicts that  $Q_G$  and  $(\Delta S_A)_G$  may decrease as temperature increases due to the progressive solution of inclusions. Ward<sup>2</sup> has found that  $Q_G$  and  $(\Delta S_A)_G$  do markedly decrease in the secondary recrystallization of cube texture copper as the melting point is approached. Also the results of Burke<sup>31</sup> show that  $Q_G$  and  $(\Delta S_A)_G$  for grain growth are much smaller for high purity than for commercial purity  $\alpha$  brass.

In primary recrystallization  $\Delta F'$  probably is very much larger with respect to  $I$  than in boundary migration processes driven by surface energy. Suppose that it is known that primary recrystallization occurs at a given temperature,  $T_1$ , at a strain of 0.02. Then if  $Z$  is proportional to  $\epsilon$ , as assumed, the inclusions should have a negligible effect in retarding boundary migration at  $T_1$  for a strain of 0.10. Thus, unless the strain energy is greatly reduced by recovery processes, inclusions should be effective in retarding boundary migration in primary recrystallization only when  $\epsilon$  is very small and  $(\Delta S_A)_G$  and  $Q_G$  calculated when  $\epsilon$  is relatively large should approach the real values. In the recrystallization of rock salt single crystals  $(\Delta S_A)_G$  and  $Q_G$  are very



Table II. Values of Entropy of Activation for Boundary Migration

| Substance                                      | Process                     | Temperature Range | Strain | $n$   | $(\Delta S_A)_L$ | $(\Delta S_A)_{G'}$ | $n\Delta S_f$ |
|------------------------------------------------|-----------------------------|-------------------|--------|-------|------------------|---------------------|---------------|
| Aluminum <sup>17</sup>                         | Primary recrystallization   | 425-540           | 0.04   | 13.3  |                  | 17                  | 36            |
| Aluminum <sup>1</sup>                          | Primary recrystallization   | 310-370           | 0.051  | 23    |                  | 55                  | 63            |
| Aluminum <sup>20</sup>                         | Grain growth                | 400-500           |        | 34    | 9.2              | 86                  | 93            |
| Rock salt <sup>20</sup>                        | Primary recrystallization   | 650-770           | ~0.1   | 8     |                  | 36                  | 55            |
|                                                | Primary recrystallization   | 400-520           | ~0.3   | 4.4   | 18.4             | 20                  | 30            |
| Copper <sup>16</sup>                           | Primary recrystallization   | 300-320           | 0.10   | 16    |                  | 39.5                | 37            |
|                                                | Primary recrystallization   | 340-360           | 0.10   | 10.3  | 14               | 13                  | 24            |
| Copper <sup>2</sup>                            | Secondary recrystallization | 900-1000          |        | 23.4  |                  | 41                  | 54            |
| Silicon ferrite <sup>10</sup>                  | Primary recrystallization   | 740-800           | 0.07   | 20.5  | 13               | 31.5                | 40.5          |
| Silver <sup>8</sup>                            | Secondary recrystallization | 433-533           |        | 10.4  | 9                | 7                   | 23            |
| $\alpha$ brass <sup>31</sup><br>(comm. purity) | Grain growth                | 450-700           |        | 21.6* |                  | 32                  | 52            |
| $\alpha$ brass <sup>31</sup><br>(high purity)  | Grain growth                | 450-850           |        | 15*   |                  | 9.6                 | 35            |

\* Entropy and heat of fusion calculated by atomic fraction averaging of corresponding constants for pure metals.

large for small strains (see Table I) and fall sharply as the strain is increased. More direct support for the hypothesis that inclusions often significantly retard boundary migration in primary recrystallization as well as in normal grain growth is furnished by the observations of Muller<sup>20</sup> that the boundaries move in spurts in the primary recrystallization of rock salt.

However, Anderson and Mehl's results on the primary recrystallization of pure aluminum show that at 625°K, for example,  $Q_G$  and  $(\Delta S_A)_G$  are practically as large for a strain of 0.10 as for a strain of 0.02. These results cannot be reconciled with the inclusion hypothesis, unless it is supposed that recovery reduces the energy of cold working to a value almost independent of strain before boundary migration begins.

### Summary

- 1—The relation between grain boundary migration rates and diffusion coefficients is derived on the basis of the absolute reaction rate theory.
- 2—It is shown that in lattice self-diffusion the free energy of activation greatly exceeds that in grain boundary migration.
- 3—A corollary of 2 is that in grain boundary migration the atomic mobility is many orders of magnitude larger than in lattice self-diffusion.
- 4—In silver the free energy of activation for grain boundary self-diffusion equals that for grain boundary migration, within the experimental uncertainty.
- 5—The apparent entropy of activation for boundary migration is much larger than for self-diffusion processes.
- 6—An explanation for the unexpectedly large entropy of activation in boundary migration processes is given based on the concept that inclusions retarding boundary migration become less effective at elevated temperature due to their solution and coalescence.

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# Effects of Manganese and Its Oxide On Desulphurization by Blast-Furnace Type Slags

by Nicholas J. Grant, Ulf Kalling, and John Chipman

THE operation of a blast furnace is dependent to an important extent upon the sulphur content of materials charged and the desired limit of sulphur in the product. It has long been known that the blast furnace is the most efficient tool for desulphurization in common use and that this efficiency is associated with the strongly reducing conditions of the hearth and is enhanced by increased basicity and fluidity of the slag. The chemical reactions of desulphurization may be studied from the viewpoint of the ratio of the process or of the final equilibrium conditions. Both kinds of studies contribute to an understanding of the process and both are included here.

A simple measure of the desulphurization power of a slag is given by the ratio:

$$\frac{\text{Pct sulphur in slag}}{\text{Pct sulphur in metal}} = \frac{(\text{Pct S})}{[\text{Pct S}]}$$

This ratio was used by Holbrook and Joseph<sup>1, 2</sup> to measure relative desulphurizing powers under controlled laboratory conditions. It was also used by Hatch and Chipman<sup>3</sup> as a measure of the equilibrium distribution. For the latter purpose it would be preferable to employ thermodynamic activities rather than percentages, but until very recently this has been impossible for lack of data. Now, thanks to the work of Morris and Williams<sup>4</sup> and Morris and Buehl,<sup>5</sup> the effects of carbon and silicon upon the activity of sulphur in the metal are known. The confirmation of this work and its extension to include the effects of other elements by Sherman and Chipman<sup>6</sup> and by Rosenqvist and Cox<sup>7</sup> make it possible to calculate the activity of sulphur in pig iron of any composition. Hence it is now possible to use data on the equilibrium distribution of sulphur to find its activity in the liquid slag and to approach an ultimate solution of the thermodynamic aspects of the problem.

The rate of transfer of sulphur from metal to slag is the problem of major industrial importance and indeed the principal need for equilibrium data has been as a necessary adjunct to the kinetic studies. The rate of approach to equilibrium under laboratory conditions seems slow compared to the requirements of industrial practice, and it is clear that further laboratory studies of rates are needed.

In the research reported below, the items which were investigated were the following: 1—The role of mechanical stirring on the approach to equilibrium. 2—The role of MgO in desulphurization as compared to CaO. 3—The role of MnO in desulphurization. 4—The limiting reactions which constitute the slow steps in desulphurization.

## Experimental Procedure

The experimental set-up and procedure previously described by Hatch and Chipman<sup>3</sup> were essentially followed with several small modifications. The graphite crucible containing the slag and metal charge was altered to provide considerably more

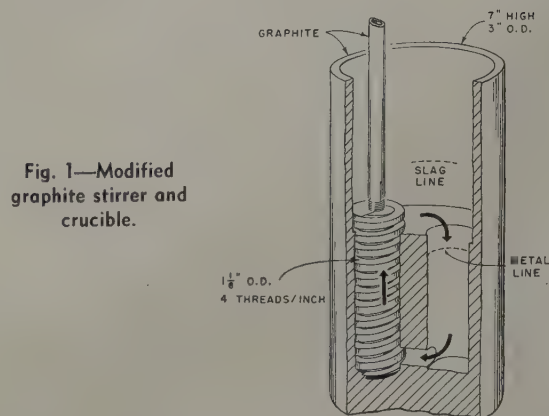


Fig. 1—Modified graphite stirrer and crucible.

active stirring and mixing of the slag and metal in the carbon monoxide atmosphere. For this purpose the crucible was machined to provide two deep cylindrical wells which were interconnected at top and bottom as shown in Fig. 1. A graphite screw with a flat thread and of shallow pitch (4 threads per in.) spinning at 600 to 800 rpm was used to lift the slag and metal over the partition between the two wells and throw them over into the second well, where the metal settled through the slag into the reservoir at the bottom. It was possible to see actual particles of slag and metal being thrown over the partition. In this respect, the stirring was more vigorous than used in the work of Hatch and Chipman.

A charge of 400 g of wash metal was first melted, and 20 g of FeS was then added to yield a bath containing 1.65 pct S. Immediately 400 g of slag (as pure mixed oxides) was added and fused. The slag was generally fused in 1 hr  $\pm$  10 min. Within 30 to 45 min after melting, the temperature was adjusted to 1525°C, and the first slag and metal samples were taken. The slag was picked up on the end of a cold Armco iron rod, whereas the metal was sucked into a silica tube.

The wash metal composition was (in percent): 4.29 C; 0.022 S; 0.021 P; 0.38 Si. The slags used were of four fixed starting compositions covering a wide range of acid-base ratios shown in Table I. Deliberate variations in MgO were made in these slags to check the role of MgO in blast-furnace desulphurization. Changes due to additions and reactions were followed by analysis of samples.

Additions of Mn and MnO were made to most of the heats to note the role of Mn and MnO on desulphurization. Three heats (62 through 64) were made in an open pot induction crucible (graphite) using a

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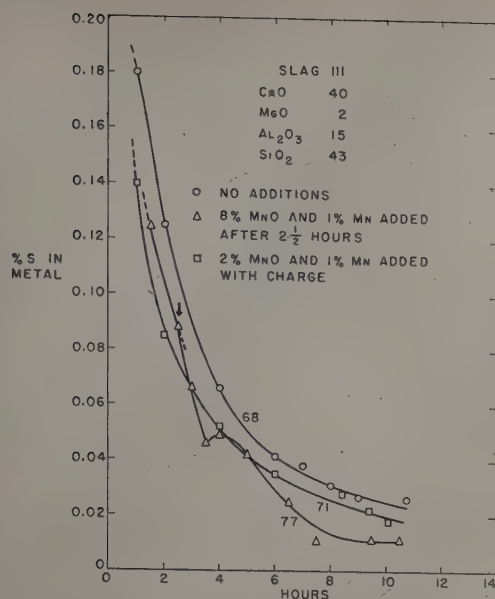
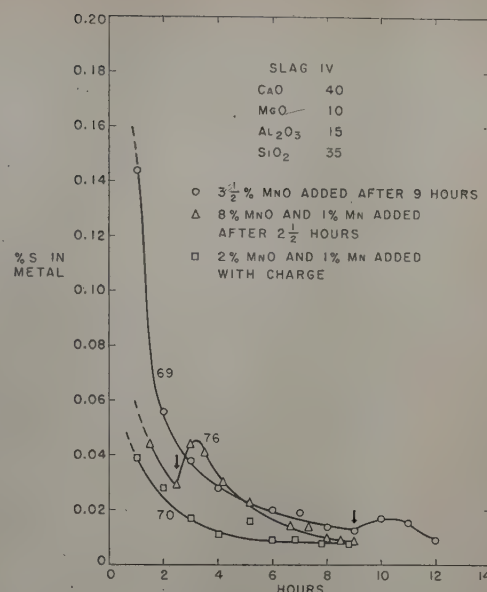


Fig. 2 (left)—Desulphurization of iron by slag III at 1525°C as a function of time.

Fig. 3 (right)—Desulphurization of iron by slag IV at 1525°C as a function of time.



slag virtually free of  $\text{SiO}_2$  to study the role of Si and  $\text{SiO}_2$  on desulphurization. A carbon monoxide atmosphere at an excess pressure of  $\frac{1}{2}$  to 1 in. of water was kept constantly over the melt.

Optical temperatures were read frequently throughout the course of a heat by sighting down the graphite tube (stirring shaft) to which the immersed stirrer head was attached. Periodic checks with a platinum thermocouple established the temperature errors to be  $\pm 5^\circ\text{C}$ , and deviation from  $1525^\circ$  during a run seldom exceeded this figure.

The stirrer was started as soon as the slag was molten, and this point was taken as zero time.

The compositions of the slag and metal samples are shown in Table II. Table III shows the nature and the time of the additions made to each slag.

**The Effect of Slag Basicity:** The sulphur content of the metal is plotted against the heat time at  $1525^\circ\text{C}$  for each grade of slag in Figs. 2 to 5 with Fig. 2 being slag III, the most acid and Fig. 5 being slag II, the most basic. Zero time is the time when the slag is first judged to be molten. For heats 66 through 80 the time from "start to add cold slag" to "slag molten" ranged from 35 to 65 min except heat 73 which took 120 min.

In each of Figs. 2 to 5 there is a "no addition" heat and these are compared in Fig. 6 from which it is very apparent that the basicity of the slag is an extremely important factor in controlling the speed of the desulphurization reactions and the final sulphur content of the metal. An approximate relationship between basicity, as measured by "Excess  $\text{CaO}$ " and the time required to reach equilibrium is shown in Table IV.

**Effect of Stirring:** While there is no direct measure of the difference in stirring effectiveness in the present heats compared to those of Hatch and Chipman,<sup>9</sup> it is believed from observations that the present stirring method was much more vigorous. Nevertheless, the time to reach sulphur equilibrium

for similar heats of the acid type in both groups of experiments was of the same order, indicating that for these rather fluid slags the added surface content was not too important a factor in the speed of the reactions. The initial desulphurization rate for all slags must be unusually high since the metal contains 1.65 pct S at the start and drops to the levels shown as the first values in Figs. 2 to 5 in 1 to 2 hr.

**Role of MnO in Blast-Furnace Slags:** Figs. 2 to 5 show the effects of Mn and MnO when added to the initial charge or during the course of a heat. The arrow in each figure shows the time of the addition. When added during the heat, a very interesting and important effect is noted in that immediately after the addition of MnO there is for each slag and in every instance a reversion of sulphur into the metal. These 4 heats are shown in Fig. 7. The full extent of the reversion is not accurately determined because a sufficient number of samples were not taken during this period.

The cause of the sulphur reversion can be ascribed but to one effect and that is the temporary reoxidation of the slag through the reduction of MnO. This is especially interesting when it is considered that MnO is a basic oxide; the expected beneficial effect of the basic addition has been overshadowed by the adverse effect of oxidation. The same or greater effect could have been achieved by the addition of the more easily reducible oxide FeO to the slag which is known to affect adversely the desulphurizing power of slags of this type.<sup>8</sup> It will be noted that recovery of the system from the oxygen addition is more rapid the more basic the slag.

Table II shows that most of the MnO is reduced to Mn in the metal. The maximum MnO remaining in any of the heats (nonequilibrium) is only 1.3 pct in the most acid slag while Mn in the metal runs as high as 5 pct.

Of great current interest is the effect of basicity on the MnO reduction from the slag. Manganese recovery is defined as the ratio of Mn in the metal to total manganese. This ratio is plotted in Fig. 8 against Excess Base. A very similar curve was obtained using Excess  $\text{CaO}$  with about the same degree of scatter of points. Fig. 8 shows that with the most basic slags a recovery of about 96 pct of the manganese may be achieved, under near-equilibrium conditions. The most acid slag with essentially zero Excess Base shows 82 pct Mn recovery. The curve

Table I. Starting Slag Compositions

| Slag No. | CaO | MgO | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ |
|----------|-----|-----|----------------|-------------------------|
| I        | 50  | 2   | 33             | 15                      |
| II       | 50  | 10  | 25             | 15                      |
| III      | 40  | 2   | 43             | 15                      |
| IV       | 40  | 10  | 35             | 15                      |

Table II—Compositions of Slag and Metal Samples Taken at 1525°C

| Heat No.,<br>Slag No. | Sample | Time  | Metal, Wt Pct |      |       |        | Slag, Wt Pct |       |       |                  |                                |      |       |
|-----------------------|--------|-------|---------------|------|-------|--------|--------------|-------|-------|------------------|--------------------------------|------|-------|
|                       |        |       | C             | Mn   | Si    | S      | S            | CaO   | MgO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MnO  | FeO   |
| 64                    | 1      | 0:40  | —             | —    | —     | 0.006  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 2      | 1:40  | —             | —    | —     | 0.004  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 3      | 2:30  | —             | —    | —     | 0.003  | 1.15         | 50.00 | —     | 1.34             | 48.55                          | —    | 0.090 |
|                       | 4      | 3:00  | —             | —    | —     | 0.004  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 5      | 3:45  | —             | —    | —     | 0.0044 | —            | —     | —     | —                | —                              | —    | —     |
|                       | 6      | 4:20  | —             | —    | —     | 0.0045 | 1.24         | 45.87 | —     | 9.16             | 44.56                          | —    | 0.140 |
| 65 II                 | 1      | 0:25  | —             | —    | 0.07  | 0.012  | 1.66         | 48.13 | 10.24 | 25.64            | 16.32                          | —    | —     |
|                       | 2      | 1:30  | —             | —    | 0.15  | 0.008  | 1.68         | —     | —     | 25.74            | —                              | —    | —     |
|                       | 3      | 3:30  | —             | —    | —     | 0.008  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 4      | 4:30  | —             | —    | 0.22  | 0.005  | 1.68         | —     | —     | 25.52            | —                              | —    | —     |
|                       | 5      | 5:30  | —             | —    | —     | 0.0084 | —            | —     | —     | —                | —                              | —    | —     |
|                       | 6      | 6:30  | —             | —    | 0.28  | 0.004  | 1.71         | 48.79 | 9.90  | 25.48            | 15.92                          | —    | 0.025 |
| 68 III                | 1      | 1:00  | —             | —    | 0.61  | 0.18   | 1.48         | 36.20 | 2.33  | 43.18            | 17.74                          | —    | —     |
|                       | 2      | 2:00  | —             | —    | 0.96  | 0.125  | 1.54         | —     | —     | 42.60            | —                              | —    | —     |
|                       | 3      | 4:00  | —             | —    | 1.72  | 0.066  | 1.59         | —     | —     | 41.56            | —                              | —    | —     |
|                       | 4      | 6:00  | —             | —    | —     | 0.0415 | —            | —     | —     | —                | —                              | —    | —     |
|                       | 5      | 7:00  | —             | —    | 2.77  | 0.038  | 1.64         | —     | —     | 40.06            | —                              | —    | —     |
|                       | 6      | 8:00  | —             | —    | —     | 0.031  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 7      | 9:00  | —             | —    | 3.28  | 0.027  | 1.66         | —     | —     | 39.16            | —                              | —    | —     |
|                       | 8      | 10:00 | —             | —    | 3.65  | 0.026  | 1.68         | 39.21 | 2.35  | 38.56            | 16.28                          | —    | 0.072 |
| 69 IV                 | 1      | 1:00  | —             | —    | 0.19  | 0.144  | 1.55         | 34.80 | 10.38 | 35.42            | 17.08                          | —    | —     |
|                       | 2      | 2:00  | —             | —    | 0.32  | 0.056  | 1.64         | —     | —     | 35.20            | —                              | —    | —     |
|                       | 3      | 3:00  | —             | —    | 0.50  | 0.038  | 1.65         | —     | —     | 35.08            | —                              | —    | —     |
|                       | 4      | 4:15  | —             | —    | 0.78  | 0.028  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 5      | 6:15  | —             | —    | 1.12  | 0.020  | 1.67         | —     | —     | 34.20            | —                              | —    | —     |
|                       | 6      | 7:15  | —             | —    | 1.23  | 0.019  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 7      | 8:15  | —             | —    | 1.32  | 0.014  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 8      | 9:15  | —             | —    | 1.45  | 0.0126 | 1.72         | —     | —     | 33.60            | —                              | —    | —     |
|                       | 9      | 10:15 | —             | 1.39 | 1.19  | 0.017  | —            | —     | —     | —                | —                              | 1.26 | 0.123 |
|                       | 10     | 11:15 | —             | 1.79 | 1.26  | 0.0155 | —            | —     | —     | —                | —                              | 0.70 | 0.073 |
|                       | 11     | 12:15 | —             | 1.84 | 1.28  | 0.009  | 1.67         | 38.30 | 10.07 | 34.20            | 14.78                          | 0.51 | 0.071 |
| 70 IV                 | 1      | 1:00  | 5.06          | 1.38 | 0.22  | 0.039  | —            | —     | —     | —                | —                              | 0.87 | 0.132 |
|                       | 2      | 2:00  | 4.88          | 1.60 | 0.67  | 0.028  | —            | —     | —     | —                | —                              | 0.64 | —     |
|                       | 3      | 3:00  | 4.82          | 1.77 | 1.05  | 0.017  | —            | —     | —     | —                | —                              | 0.46 | —     |
|                       | 4      | 4:00  | 4.75          | 1.81 | 1.25  | 0.011  | —            | —     | —     | —                | —                              | 0.46 | —     |
|                       | 5      | 5:10  | 4.50          | —    | 1.50  | 0.020  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 6      | 6:00  | 4.64          | 1.81 | 1.54  | 0.009  | —            | —     | —     | —                | —                              | —    | 0.086 |
|                       | 7      | 6:50  | —             | —    | 1.67  | 0.010  | —            | —     | —     | —                | —                              | —    | 0.080 |
|                       | 8      | 7:50  | 4.73          | 1.84 | 1.74  | 0.009  | —            | —     | —     | —                | —                              | 0.37 | 0.072 |
|                       | 9      | 8:50  | 4.64          | 1.87 | 1.81  | 0.009  | 1.65         | 39.61 | 10.16 | 33.60            | 17.90                          | 0.31 | —     |
| 71 III                | 1      | 1:00  | —             | —    | 0.57  | 0.14   | —            | —     | —     | —                | —                              | —    | —     |
|                       | 2      | 2:00  | —             | —    | 1.15  | 0.085  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 3      | 4:00  | —             | —    | 1.68  | 0.052  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 4      | 6:05  | —             | —    | 2.16  | 0.035  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 5      | 7:00  | —             | —    | 2.44  | 0.041  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 6      | 8:30  | —             | —    | 3.19  | 0.028  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 7      | 9:30  | —             | —    | 3.65  | 0.022  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 8      | 10:15 | —             | —    | —     | 0.018  | —            | —     | —     | —                | —                              | —    | —     |
| 72 I                  | 1      | 0:30  | 5.13          | 1.35 | 0.21  | 0.027  | —            | —     | —     | —                | —                              | 0.89 | —     |
|                       | 2      | 1:00  | —             | 1.49 | —     | 0.017  | —            | —     | —     | —                | —                              | 0.57 | —     |
|                       | 3      | 2:00  | 5.08          | 1.56 | 0.48  | 0.011  | —            | —     | —     | —                | —                              | 0.57 | —     |
|                       | 4      | 3:00  | 5.02          | 1.63 | 0.63  | 0.008  | —            | —     | —     | —                | —                              | 0.38 | 0.115 |
|                       | 5      | 4:00  | 5.00          | 1.80 | 0.72  | 0.010  | —            | —     | —     | —                | —                              | 0.36 | 0.071 |
|                       | 6      | 5:00  | —             | 1.82 | —     | 0.010  | —            | —     | —     | —                | —                              | 0.34 | 0.074 |
|                       | 7      | 6:00  | 4.95          | 1.93 | 1.17  | 0.008  | 1.61         | —     | —     | 32.60            | —                              | 0.33 | 0.097 |
|                       | 8      | 7:00  | —             | 2.62 | —     | 0.009  | —            | —     | —     | —                | —                              | 1.11 | 0.082 |
|                       | 9      | 8:00  | —             | 3.15 | —     | 0.0085 | —            | —     | —     | —                | —                              | 0.64 | 0.068 |
|                       | 10     | 10:00 | 4.93          | 3.26 | 1.08  | 0.007  | 1.61         | 47.98 | 2.06  | 32.14            | 15.72                          | 0.52 | 0.090 |
| 73 II                 | 1      | 0:15  | 5.12          | 1.41 | 0.06  | 0.016  | 1.63         | 47.15 | 9.39  | 26.06            | 15.62                          | 0.64 | —     |
|                       | 2      | 0:40  | 4.99          | 1.62 | —     | 0.006  | 1.70         | —     | —     | 26.56            | —                              | 0.34 | —     |
|                       | 3      | 1:40  | 5.15          | 1.88 | 0.11  | 0.006  | 1.74         | —     | —     | 26.14            | —                              | 0.14 | —     |
|                       | 4      | 2:40  | —             | 1.85 | —     | 0.005  | —            | —     | —     | —                | —                              | 0.16 | —     |
|                       | 5      | 3:40  | —             | 1.77 | —     | 0.004  | —            | —     | —     | —                | —                              | 0.08 | —     |
|                       | 6      | 4:40  | 5.18          | 2.96 | 0.11  | 0.004  | 1.68         | —     | —     | 26.82            | —                              | 0.30 | —     |
|                       | 7      | 5:40  | —             | —    | —     | 0.004  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 8      | 6:40  | 5.09          | 3.42 | 0.22  | 0.004  | 1.65         | 47.21 | 9.75  | 26.20            | 16.50                          | 0.25 | 0.087 |
| 74 I                  | 1      | 0:30  | —             | —    | 0.14  | 0.037  | 1.67         | 47.29 | 2.33  | 33.80            | 17.42                          | —    | 0.187 |
|                       | 2      | 0:65  | —             | —    | 0.32  | 0.022  | 1.63         | —     | —     | 33.88            | —                              | —    | —     |
|                       | 3      | 1:65  | —             | —    | —     | 0.015  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 4      | 2:65  | —             | —    | 0.88  | 0.015  | 1.64         | —     | —     | 33.16            | —                              | —    | —     |
|                       | 5      | 4:10  | —             | —    | 1.19  | 0.0084 | 1.65         | —     | —     | 32.72            | —                              | —    | —     |
|                       | 6      | 5:10  | —             | —    | —     | 0.009  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 7      | 6:10  | —             | —    | —     | 0.007  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 8      | 7:10  | —             | —    | 1.47  | 0.007  | 1.66         | 49.41 | 2.41  | 32.08            | 15.58                          | —    | 0.058 |
| 75 I                  | 1      | 0:30  | —             | —    | —     | 0.029  | —            | —     | —     | —                | —                              | —    | 0.109 |
|                       | 2      | 1:30  | —             | —    | —     | 0.021  | —            | —     | —     | —                | —                              | —    | 0.160 |
|                       | 3      | 2:00  | —             | 4.01 | —     | 0.025  | —            | —     | —     | —                | —                              | 3.60 | 0.138 |
|                       | 4      | 2:35  | —             | 4.12 | —     | 0.021  | —            | —     | —     | —                | —                              | 2.80 | 0.150 |
|                       | 5      | 2:65  | —             | 4.41 | —     | 0.014  | —            | —     | —     | —                | —                              | 2.36 | 0.125 |
|                       | 6      | 3:65  | —             | 4.71 | —     | 0.0135 | —            | —     | —     | —                | —                              | 1.80 | 0.127 |
|                       | 7      | 4:65  | —             | 4.87 | —     | 0.011  | —            | —     | —     | —                | —                              | 1.47 | 0.122 |
|                       | 8      | 5:65  | —             | 5.04 | —     | 0.007  | —            | —     | —     | —                | —                              | 1.23 | 0.075 |
|                       | 9      | 6:65  | —             | 5.10 | —     | 0.0054 | —            | —     | —     | —                | —                              | 0.95 | 0.089 |
|                       | 10     | 7:65  | —             | 5.08 | —     | 0.0064 | —            | —     | —     | —                | —                              | 0.80 | 0.124 |
|                       | 11     | 8:50  | 4.97          | 5.32 | 0.94  | 0.0067 | 1.50         | 48.30 | 2.07  | 32.52            | 16.08                          | 0.87 | 0.105 |
|                       | 12     | 9:20  | —             | 4.93 | —     | —      | —            | —     | —     | —                | —                              | 0.82 | 0.102 |
| 76 IV                 | 1      | 1:30  | —             | —    | —     | 0.044  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 2      | 2:30  | —             | —    | —     | 0.029  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 3      | 3:00  | —             | 3.65 | —     | 0.044  | —            | —     | —     | —                | —                              | —    | —     |
|                       | 4      | 3:30  | —             | 4.03 | —     | 0.041  | —            | —     | —     | —                | —                              | 2.60 | —     |
|                       | 5      | 4:10  | —             | 4.36 | —     | 0.030  | —            | —     | —     | —                | —                              | 2.63 | —     |
|                       | 6      | 5:10  | —             | 4.38 | 0.023 | 0.023  | —            | —     | —     | —                | —                              | 2.22 | —     |
|                       | 7      | 6:40  | —             | 4.51 | —     | 0.014  | —            | —     | —     | —                | —                              | 1.88 | 0.107 |
|                       | 8      | 7:20  | —             | 4.72 | —     | 0.014  | —            | —     | —     | —                | —                              | 1.35 | —     |
|                       | 9      | 8:00  | —             | 4.84 | —     | 0.010  | —            | —     | —     | —                | —                              | 1.21 | 0.080 |
|                       | 10     | 8:30  | —             | 4.97 | —     | 0.009  | —            | —     | —     | —                | —                              | 1.14 | 0.055 |
|                       | 11     | 9:00  | —             | 5.07 | 1.37  | 0.009  | 1.61         | 39.30 | 9.87  | 33.38            | 14.52                          | 0.92 | 0.065 |



Table II (Cont.)—Compositions of Slag and Metal Samples Taken at 1525°C

| Heat No.,<br>Slag No. | Sample | Time  | Metal, Wt Pct |       |      |        | Slag, Wt Pct |       |       |                  |                                |       |       |
|-----------------------|--------|-------|---------------|-------|------|--------|--------------|-------|-------|------------------|--------------------------------|-------|-------|
|                       |        |       | C             | Mn    | Si   | S      | S            | CaO   | MgO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MnO   | FeO   |
| 77 III                | 1      | 1:30  | —             | —     | —    | 0.124  | —            | —     | —     | —                | —                              | —     | —     |
|                       | 2      | 2:30  | —             | —     | —    | 0.088  | —            | —     | —     | —                | —                              | —     | —     |
|                       | 3      | 3:05  | —             | 1.14  | —    | 0.066  | —            | —     | —     | —                | —                              | 3.64  | —     |
|                       | 4      | 3:35  | —             | 3.46  | —    | 0.046  | —            | —     | —     | —                | —                              | 3.34  | —     |
|                       | 5      | 4:05  | —             | 3.27  | —    | 0.049  | —            | —     | —     | —                | —                              | 3.06  | —     |
|                       | 6      | 5:05  | —             | 3.89  | —    | 0.042  | —            | —     | —     | —                | —                              | 2.59  | —     |
|                       | 7      | 6:35  | —             | 4.29  | —    | 0.025  | —            | —     | —     | —                | —                              | 2.17  | —     |
|                       | 8      | 7:35  | —             | 4.26  | —    | 0.011  | —            | —     | —     | —                | —                              | 2.01  | —     |
|                       | 9      | 8:35  | —             | —     | —    | 0.019  | —            | —     | —     | —                | —                              | —     | —     |
|                       | 10     | 9:35  | —             | —     | —    | 0.0115 | —            | —     | —     | —                | —                              | —     | —     |
|                       | 11     | 10:35 | 4.13          | 4.66  | 3.46 | 0.0115 | 1.50         | 41.51 | 2.21  | 37.90            | 17.76                          | 1.32  | 0.094 |
| 79 II                 | 1      | 0:25  | —             | —     | —    | 0.004  | —            | —     | —     | —                | —                              | —     | —     |
|                       | 2      | 0:50  | —             | —     | —    | 0.004  | —            | —     | —     | —                | —                              | —     | —     |
|                       | 3      | 1:15  | —             | —     | 0.40 | 0.004  | 1.65         | 48.00 | 10.03 | 25.72            | 15.06                          | —     | 0.132 |
| 80 II                 | 1      | 0:05  | —             | 0.015 | —    | 0.028  | —            | —     | —     | —                | —                              | 0.056 | —     |
|                       | 2      | 0:20  | —             | 0.038 | —    | 0.006  | —            | —     | —     | —                | —                              | 0.014 | —     |
|                       | 3      | 0:40  | —             | 3.04  | —    | 0.015  | —            | —     | —     | —                | —                              | 4.86  | —     |
|                       | 4      | 1:00  | —             | 3.93  | —    | 0.010  | —            | —     | —     | —                | —                              | 2.93  | —     |
|                       | 5      | 1:20  | —             | 4.37  | —    | 0.0065 | —            | —     | —     | —                | —                              | 1.80  | —     |
|                       | 6      | 1:50  | —             | 4.82  | —    | 0.005  | —            | —     | —     | —                | —                              | 1.13  | —     |
|                       | 7      | 3:00  | —             | 5.08  | —    | 0.0044 | —            | —     | —     | —                | —                              | 0.63  | —     |
|                       | 8      | 4:00  | —             | 5.14  | —    | 0.0044 | —            | —     | —     | —                | —                              | 0.55  | —     |
|                       | 9      | 5:00  | 5.21          | 5.24  | 0.22 | 0.0046 | 1.66         | 46.41 | 11.56 | 26.80            | 13.72                          | 0.44  | 0.135 |

shown in Fig. 8 does not represent equilibrium values, since MnO was still in the process of being reduced as shown in Fig. 9.

The effect of manganese on both desulphurization rate and equilibrium is very small and is confined to the two less basic slags. Disregarding the heats in which MnO was added during the experiment and considering only those in which Mn and MnO were included in the charge, the curves of the most acid slags shown in Figs. 2 and 3 indicate that the time required to reach a given sulphur level is slightly shortened by the addition. At the same time the final distribution is slightly improved; this is evident in the most acid slag where the effect is greatest.

If the "manganese recovery ratio" is plotted against time, the curves shown in Fig. 9 for the 4 types of slags are obtained. These curves show the approach to manganese equilibrium with time as a function of basicity. As would be expected, the most basic slag (II) approaches equilibrium most rapidly, but even at 96 pct recovery has not reached equilibrium. The break in the curves for slags II and IV is due to a 2 pct MnO addition to the slag, and shows that the MnO is rapidly reduced. Heat 77 (slag III) did not have Mn and MnO charged initially as did the others and so does not have the same "zero."

The curves of Fig. 9 are almost a mirror image of the curves of Figs. 6 and 7 for desulphurization, the

transfer of manganese and sulphur being in opposite directions. This suggests that MnO in the slag or the manganese recovery ratio might be a useful indicator for estimating the basicity of the slag but especially its degree of oxidation.

FeO is too easily reduced, leaving quantities of less than 0.1 pct in the slag. Such a small amount is too difficult to analyze correctly. MnO, on the other hand, is less readily reduced than FeO, is more easily analyzed, and approaches equilibrium in about the same time as sulphur.

Values of "manganese recovery ratio" for the blast furnace strongly suggest that in the blast furnace the slags are not as thoroughly reduced as the slags reported in this research (for a given basicity). This would correspond to a higher degree of oxidation of the slag, causing the lower desulphurization ratios noted in the blast furnace compared to comparable basic slags reported in this work.

**Effect of MgO:** One of the aims of this research was to establish the effect of MgO on the desulphurizing power of the slag. For this purpose the starting slags were made up with 2 or 10 pct MgO. Since the principal desulphurizing oxide is known to be CaO, the subsidiary effect of MgO can be found by comparing slags with or without this component. The comparison is shown in Fig. 10 where the ratio (pct S)/[pct S] in the final samples is plotted against

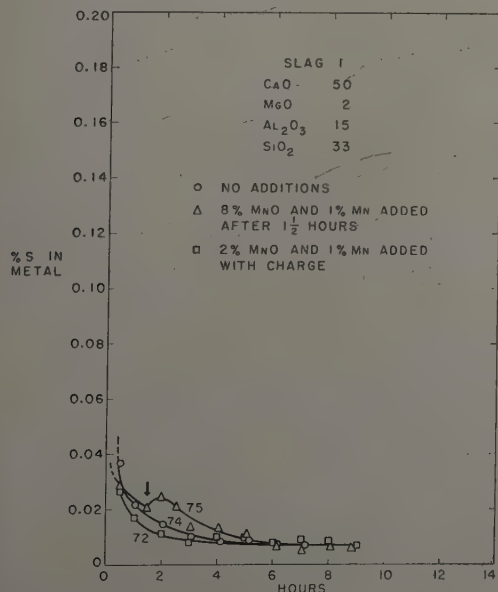
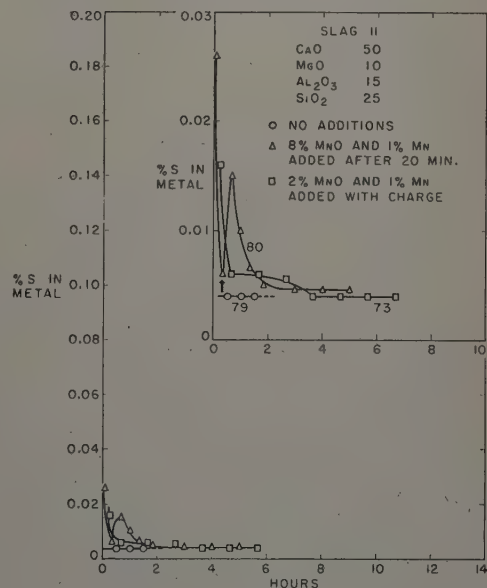


Fig. 4 (left)—Desulphurization of iron by slag I at 1525°C as a function of time.

Fig. 5 (right)—Desulphurization of iron by slag II at 1525°C as a function of time. Inset based on expanded sulphur scale.



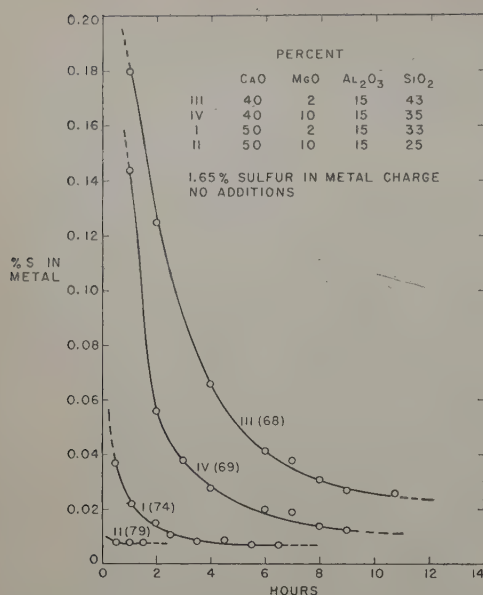
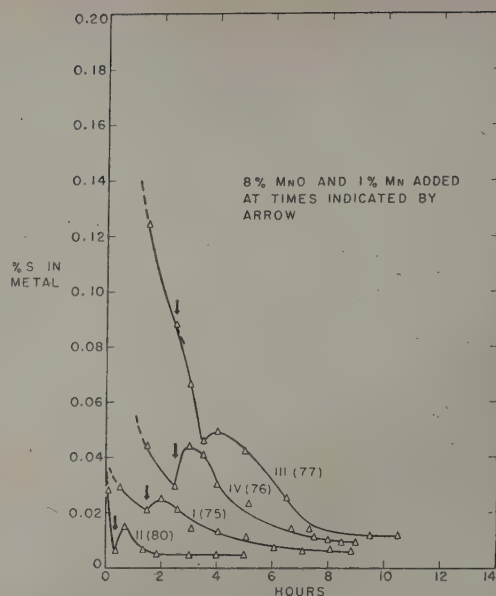


Fig. 6 (left)—Comparison of slags I to IV showing pronounced effect of slag basicity on rate of sulphur removal and final sulphur. All "no addition" heats.

Fig. 7 (right)—Comparison of slags I to IV wherein Mn and MnO are added during the heat.



Excess Base. The latter is defined here as the excess number of mols of  $\text{CaO} + \text{MgO}$ , per mol of slag, over and above that required to form compounds of the type  $\text{CaSiO}_3$  and  $\text{CaAl}_2\text{O}_4$ . The straight line is taken from Sherman and Grant's<sup>9</sup> treatment of Hatch and Chipman's<sup>8</sup> data, adjusted slightly for the difference in temperature. The points for 2 pct MgO fall slightly below this line, those for 10 pct considerably below. The one point for a simple lime-alumina slag is on the line.

Fig. 11 is a plot of the same points as in Fig. 10 except that basicity is expressed as "Excess CaO" as defined by Sherman and Grant.<sup>9</sup> The solid line is the same line as the Zero MgO line of Fig. 10; and it is to be noted that the points fall uniformly about this line within the limits of an error of 0.001 pct S in the metal which is represented by the dashed lines. For comparison, the curve at 1500°C based on the work of Hatch and Chipman is also included (dotted line).

There is no preferential grouping of points in Fig. 11 on the basis of MgO content. Thus Figs. 10 and 11 confirm that whereas MgO is equal to CaO on a molar basis in the neutralization of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , only CaO is truly effective in the desulphurization of iron.<sup>9</sup> It should be added that the term Excess CaO merely serves as an approximate measure of CaO activity in the range of compositions for which it is used.

The simple sulphur ratio in weight percent has

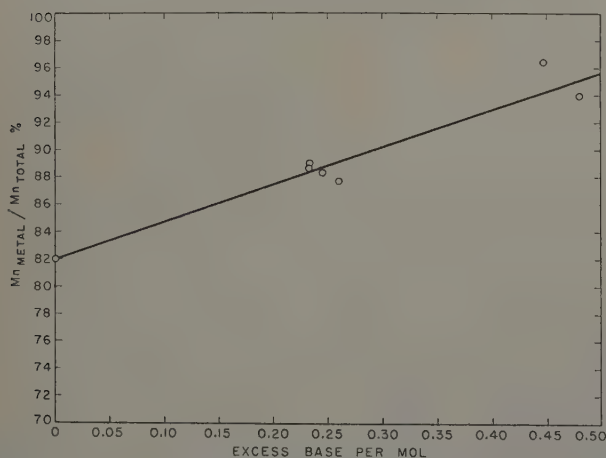


Fig. 8—Manganese recovery as a function of Excess Base at 1525°C.

been used throughout this work. This was desirable first because a direct comparison was permitted with the results published by Hatch and Chipman,<sup>8</sup> and second because the data on sulphur activity in the metal in the presence of other elements is not yet complete.

**Factors Affecting the Rate of Desulphurization:** Recently, Derge, Philbrook and Goldman<sup>10</sup> suggested that of three probable reactions applicable to desulphurization occurring in the blast furnace, the limiting reactions were the heterogeneous reactions involving the transfer of Fe and S to the slag and the reduction of FeO from the slag by C.

The present research indicates that this is only true to a limited extent, but that other factors are operative which previously had not been investigated thoroughly enough. It is noted that:

1—Fig. 6 shows the profound effect of basicity on the desulphurization rate which suggests that the C plus FeO reaction is in turn controlled by other reactions.

2—Fig. 7 shows the rapid response of metal sulphur to oxygen and its equally rapid recovery from the effect of oxygen (from MnO) in all slags regardless of basicity.

Table III. Nature of Additions Made to Each Heat

| Heat | Slag                               | Additions to Slag or Metal*                  |
|------|------------------------------------|----------------------------------------------|
| 68   | III                                | No additions                                 |
| 77   | III                                | 4 g Mn and 32 g MnO added after sample 2     |
| 71   | III                                | 4 g Mn and 8 g MnO added with initial charge |
| 69   | IV                                 | 11 g MnO added after sample 8                |
| 76   | IV                                 | 4 g Mn and 32 g MnO added after sample 2     |
| 70   | IV                                 | 4 g Mn and 8 g MnO added with initial charge |
| 74   | I                                  | No additions                                 |
| 75   | I                                  | 4 g Mn and 32 g MnO added after sample 2     |
| 72   | I                                  | 4 g Mn and 8 g MnO added to initial charge   |
|      |                                    | 8 g MnO added after sample 7                 |
| 66   | II                                 | No additions                                 |
| 79   | II                                 | No additions                                 |
| 80   | II                                 | 4 g Mn and 30 g MnO added after sample 2     |
| 73   | II                                 | 4 g Mn and 8 g MnO added to initial charge   |
|      |                                    | 8 g MnO added after sample 5                 |
| 64   | CaO-Al <sub>2</sub> O <sub>3</sub> | 10 g SiO <sub>2</sub> added after sample 3   |

\*Based on 400 g of metal and 400 g of slag

Table IV. Time Required to Reach Sulphur Equilibrium

| Slag | Heat | Excess CaO | Approximate Time for S Equilibrium, Hr |
|------|------|------------|----------------------------------------|
| III  | 68   | none       | 12                                     |
| IV   | 69   | 0.185      | 10-12                                  |
| I    | 74   | 0.253      | 6                                      |
| II   | 79   | 0.365      | 1                                      |



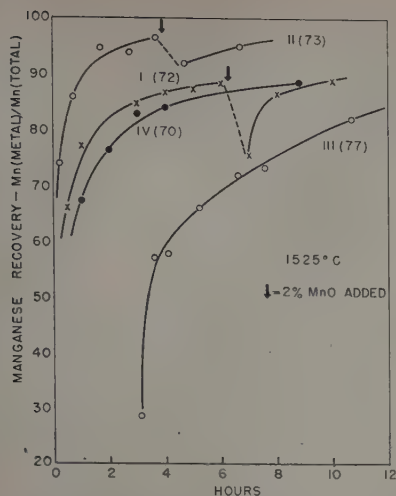


Fig. 9—Manganese recovery as a function of time for slags I to IV at 1525°C.

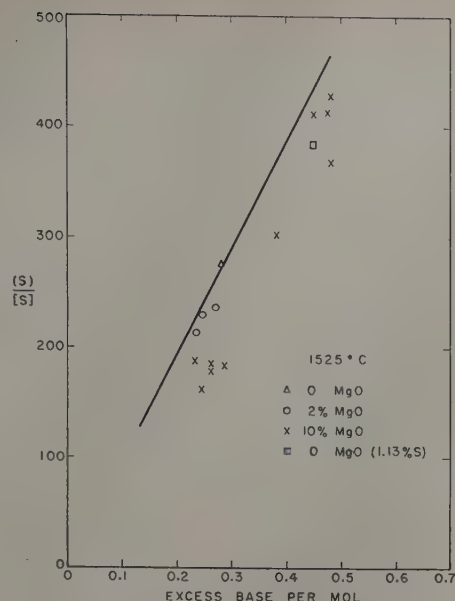


Fig. 10—Desulphurization ratio vs. Excess Base at 1525°C comparing 2 and 10 pct MgO slags relative to the zero MgO line for slags of 1.65 pct S.

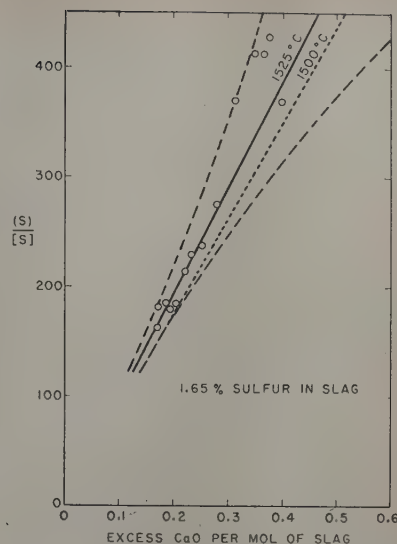


Fig. 11—Desulphurization ratio vs. Excess CaO at 1525°C showing 0.001 pct S limits. Dotted curve for 1500°C.

3—A large increase in stirring efficiency did not materially increase desulphurization rates in the slower more easily observable acid heats.

These observations coupled with an examination of the analytical values in Table II suggested  $\text{SiO}_2$  reduction might in fact be the controlling reaction.

Accordingly, a heat was made using a slag composed of 50 pct by weight of both  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ , a slag virtually free of  $\text{SiO}_2$  or other reducible oxides. This heat, No. 64, shows that for a slag with Excess  $\text{CaO}$  of 0.442 the iron was completely desulphurized in less than 40 min from the time of the first, unfused, cold slag addition. The heat was made in a graphite crucible open to the air and therefore was not made under as ideal reducing conditions as the other heats. A very violent gas evolution accompanied the desulphurization reaction the moment the slag and metal were stirred.

From the above it would appear that it is not the C and  $\text{FeO}$  reaction which makes the desulphurization process slow. Instead it is the slow reduction of  $\text{SiO}_2$ . This reduction shifts the slag composition to greater basicity which tends to promote the desulphurization reactions but at the same time provides oxygen to the slag which prevents efficient desulphurization. The speed of the desulphurization reaction is directly related to the degree of oxidation of the slag. Easily reducible oxides such as  $\text{FeO}$  offer little impediment to desulphurization, whereas oxides such as the more refractory  $\text{SiO}_2$  release oxygen slowly, maintaining an oxidized slag over a long period of time. This role of  $\text{SiO}_2$  reduction on the desulphurization reactions is to be the subject of a separate research program.

### Conclusions

1—Increased vigor of stirring the slag and metal has little effect on increasing the rate of desulphurization of iron for the more acid slags.

2— $\text{MnO}$  is readily reduced, reaching a reduction efficiency of 96 pct or more for the most basic slags.  $\text{MnO}$  remains in such small amounts in the slag that its influence is difficult to measure except in the most acid heats where it appears to increase the rate of desulphurization slightly.

3—Oxygen (from  $\text{MnO}$ ) causes an almost immediate sulphur reversion into the metal. The slag recovers more slowly. The response is more rapid the more basic the slag.

4—Manganese equilibrium is achieved more slowly than sulphur equilibrium but is of comparable time. Manganese recovery may serve as an indication of the degree of slag oxidation.

5—The two most important factors on the speed of desulphurization and on the final sulphur in the metal are the basicity of the slag and the degree of oxidation of the slag.

6—The basicity is best expressed by the value Excess  $\text{CaO}$ .

7— $\text{MgO}$  is a poor desulphurizer but can replace  $\text{CaO}$  in neutralizing the acid constituents.

8—The limiting reaction in controlling the rate of desulphurization is probably the reduction of  $\text{SiO}_2$  and not the heterogeneous reaction between C and  $\text{FeO}$ .

### Acknowledgments

The authors express their thanks to the American Iron and Steel Institute who sponsored this research program. They are grateful to Olaf Troili who participated in making all the experimental heats and especially to Charles W. Sherman for his many calculations and active participation throughout the program.

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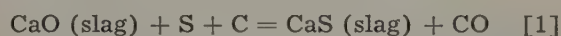
- <sup>1</sup> Holbrook and Joseph: *Trans. AIME* (1936) **120**, p. 99.
- <sup>2</sup> Holbrook: *Trans. AIME* (1938) **131**, p. 127.
- <sup>3</sup> Hatch and Chipman: *Trans. AIME* (1949) **185**, p. 274; *JOURNAL OF METALS* (April 1949).
- <sup>4</sup> Morris and Williams: *Trans. ASM* (1949) **41**, p. 1425.
- <sup>5</sup> Morris and Buehl: *Trans. AIME* (1950) **188**, p. 317; *JOURNAL OF METALS* (February 1950).
- <sup>6</sup> Sherman and Chipman: In preparation.
- <sup>7</sup> Rosenqvist and Cox: *Trans. AIME* (1950) **188**, p. 1389; *JOURNAL OF METALS* (November 1950).
- <sup>8</sup> Rocca, Grant and Chipman: *JOURNAL OF METALS* (April 1951) *Trans. AIME*, p. 319.
- <sup>9</sup> Sherman and Grant: *Trans. AIME* (1949) **185**, p. 898; *JOURNAL OF METALS* (November 1949).
- <sup>10</sup> Derge, Philbrook and Goldman: *Trans. AIME* (1950) **188**, p. 1111; *JOURNAL OF METALS* (September 1950).

# Effect of Silica Reduction on the Desulphurizing Power Of Blast-Furnace Type Slags

by Nicholas J. Grant, Olaf Troili, and John Chipman

IN recent studies of the factors which affect the rate of desulphurization and its equilibrium, it became apparent that certain concurrent reactions were operative which had a significant effect on desulphurization. This is emphasized in the experiments of Hatch and Chipman<sup>1</sup> and of Grant, Kalling, and Chipman<sup>2</sup> by the slow approach to a final state of equilibrium which is in marked contrast to the initial rapid transfer of sulphur from metal to slag. Since the removal of sulphur is of such profound importance in iron and steelmaking, it appeared necessary to investigate the reactions responsible for this behavior.

It is now known that the presence of iron oxide in the slag interferes seriously with the principal reaction of blast-furnace desulphurization:



The interfering reaction is most simply expressed as:



and a small concentration of oxygen (or FeO) is sufficient to hold a considerable amount of sulphur in the metal.

It has been shown by Grant, Kalling, and Chipman<sup>2</sup> that the addition of MnO to blast-furnace slag slows the removal of sulphur from the metal. This effect overshadows the contribution of MnO to basicity and is ascribed to its oxidizing power.

It will be shown in this paper that SiO<sub>2</sub> also has sufficient oxidizing power to interfere with blast-furnace desulphurization. This is, of course, only one of its several effects. Primarily it is an acid and therefore reduces the concentration of excess lime. But when silicon is reduced to the metal the oxygen to which it was previously bonded becomes in part available for reaction 2. The proof of this statement is found in the following experiments.

## Experimental Procedure and Results

Utilizing the same procedure and apparatus described by Grant, Kalling, and Chipman<sup>2</sup> five additional heats were made using slags IV and II, the starting compositions of which were: slag IV—40 CaO, 10 MgO, 35 SiO<sub>2</sub>, 15 Al<sub>2</sub>O<sub>3</sub>; and slag II—50 CaO, 10 MgO, 25 SiO<sub>2</sub>, 15 Al<sub>2</sub>O<sub>3</sub>.

An important difference between these heats and those previously reported was that silicon to the extent of 1 to 4 pct was added to the present heats whereas the starting silicon content was formerly about 0.2 pct.

Table I shows the slag and metal analyses for heats 82 to 87, and Table II shows the silicon addi-

Table I. Slag and Metal Analyses of Samples Taken at 1525°C

| Heat, Slag, and Sample Nos. | Time | Metal, Wt Pct |      |      | Slag, Wt Pct |      |       |                  |                                |       |
|-----------------------------|------|---------------|------|------|--------------|------|-------|------------------|--------------------------------|-------|
|                             |      | C             | Si   | S    | S            | CaO  | MgO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> |       |
| 82 IV                       | 1    | 0:30          | 4.61 | 1.75 | 0.015        | 1.64 | —     | —                | 33.52                          | —     |
|                             | 2    | 1:30          | —    | —    | 0.014        | —    | —     | —                | —                              | —     |
|                             | 3    | 2:30          | 4.63 | 2.12 | 0.0109       | 1.64 | —     | —                | 33.26                          | —     |
|                             | 4    | 3:30          | —    | —    | 0.0107       | —    | —     | —                | —                              | —     |
|                             | 5    | 4:30          | —    | —    | 0.0100       | —    | —     | —                | —                              | —     |
|                             | 6    | 5:30          | 4.40 | 2.52 | 0.0090       | 1.67 | 38.24 | 11.11            | 32.38                          | 15.20 |
|                             | 7    | 6:30          | —    | —    | 0.0094       | —    | —     | —                | —                              | —     |
| 83 IV                       | 1    | 0:30          | 4.08 | 2.73 | 0.0142       | 1.62 | —     | —                | 34.48                          | —     |
|                             | 2    | 1:00          | —    | —    | 0.0112       | —    | —     | —                | —                              | —     |
|                             | 3    | 1:30          | —    | —    | 0.0110       | —    | —     | —                | —                              | —     |
|                             | 4    | 2:30          | 3.98 | 2.88 | 0.0106       | 1.62 | —     | —                | 34.24                          | —     |
|                             | 5    | 3:30          | —    | —    | 0.0101       | —    | —     | —                | —                              | —     |
|                             | 6    | 4:30          | —    | —    | 0.0101       | —    | —     | —                | —                              | —     |
|                             | 7    | 5:30          | 4.00 | 3.05 | 0.0104       | 1.63 | 36.7  | 12.07            | 33.94                          | 15.60 |
| 84 IV                       | 1    | 0:30          | 3.80 | 3.92 | 0.013        | —    | —     | —                | 34.3                           | —     |
|                             | 2    | 1:30          | —    | —    | 0.010        | —    | —     | —                | —                              | —     |
|                             | 3    | 2:30          | —    | —    | 0.010        | —    | —     | —                | —                              | —     |
|                             | 4    | 4:30          | 3.87 | 4.14 | 0.009        | —    | —     | —                | —                              | —     |
|                             | 5    | 6:30          | —    | —    | 0.009        | —    | —     | —                | —                              | —     |
|                             | 6    | 8:30          | —    | 4.27 | 0.009        | —    | —     | —                | —                              | —     |
|                             | 7    | 9:30          | 3.73 | 4.36 | 0.009        | 1.67 | 36.35 | 11.51            | 33.4                           | 16.88 |
| 86 II                       | 1    | 0:20          | 4.69 | 1.41 | 0.0037       | 1.55 | 46.6  | 10.72            | 25.42                          | 14.82 |
|                             | 2    | 1:50          | —    | —    | 0.0031       | —    | —     | —                | —                              | —     |
|                             | 3    | 4:50          | 4.75 | 1.22 | 0.0031       | 1.59 | —     | —                | 26.36                          | —     |
|                             | 4    | 6:50          | —    | —    | 0.0026       | —    | —     | —                | —                              | —     |
|                             | 5    | 8:50          | 4.80 | 1.21 | 0.0033       | 1.61 | 46.7  | 9.64             | 26.98                          | 13.16 |
| 87 II                       | 1    | 0:30          | 4.06 | 3.59 | 0.003        | 1.50 | 44.8  | 10.49            | 27.08                          | 14.56 |
|                             | 2    | 1:30          | —    | —    | 0.003        | —    | —     | —                | —                              | —     |
|                             | 3    | 3:30          | 4.21 | 3.12 | 0.003        | 1.64 | —     | —                | 27.94                          | —     |
|                             | 4    | 6:00          | —    | —    | 0.003        | —    | —     | —                | —                              | —     |
|                             | 5    | 8:30          | —    | —    | 0.003        | —    | —     | —                | —                              | —     |
|                             | 6    | 9:15          | 4.41 | 2.59 | 0.003        | 1.62 | 44.4  | 9.93             | 28.66                          | 13.50 |

tions made to the charge. These additions are based on 400 g of metal and 400 g of slag. All heats had 1.65 pct S charged before the cold slag additions. The temperature was maintained at 1525°C.

**Rate of SiO<sub>2</sub> Reduction:** Fig. 1 shows the silicon content of the metal in contact with slag IV at 1525°C as a function of time. Heat 70 from the work of Grant, Kalling, and Chipman is included as the lowest starting silicon. It will be noted that even with 4 pct Si in the starting metal, there is an increase in silicon content with time. Heat 84 is apparently approaching silicon equilibrium very slowly. Heats 70 and 82 with very much lower starting silicon show a more rapid initial rise in silicon content but do not reach equilibrium during a long holding period.

Fig. 2 shows 3 different initial silicon contents for heats 73 (from Grant, Kalling, and Chipman) 86 and 87, in contact with slag II, the most basic slag. Heat 73 is increasing in silicon with time, whereas heat 87 with an initial silicon content of 3.7 pct shows a decrease with time. Heat 86 shows a very close approach to equilibrium. The rate of transfer of silicon from slag to metal is very slow in all of those heats, even those which are initially far from equilibrium.

<sup>1</sup>G. G. Hatch and J. Chipman: Sulphur Equilibria between Iron Blast-Furnace Slags and Metal. *Trans. AIME* (1949) 185, p. 274; *Journal of Metals* (April 1949).

<sup>2</sup>N. J. Grant, U. Kalling, and J. Chipman: Effects of Manganese and Its Oxide on Desulphurization by Blast-Furnace Type Slags. This volume, p. 666.



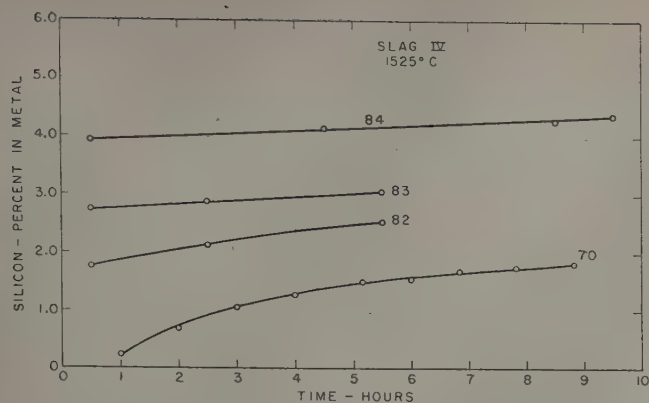


Fig. 1—Increase in silicon content of metal with time for slag IV at 1525°C.

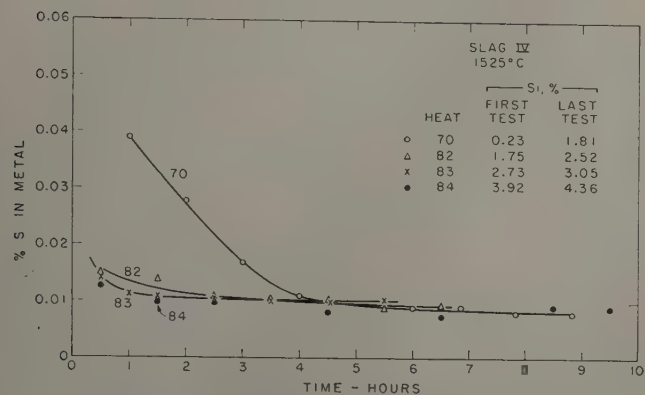


Fig. 3—Decrease in sulphur in metal with time for slag IV at 1525°C for heats of different initial silicon content.

**Effect of Silicon Content on Rate of Desulphurization and on Sulphur Equilibrium:** Figs. 3 and 4 show curves of sulphur in the metal vs. time at 1525°C for the same heats as in Figs. 1 and 2. Fig. 3 is for the more acid slag IV. It is very obvious that the addition of silicon to the charge affects profoundly the rate of sulphur removal. The effect on final sulphur is apparently smaller than the experimental uncertainties. The direct effect of silicon in the charge is to prevent or minimize the reduction of silicon from the slag thus depriving the silica of its oxidizing power.

Fig. 4 is for the very basic slag II, using an expanded ordinate of twice that of Fig. 3. For this slag also there is an effect on the desulphurization rate due to an initial high silicon content of the molten iron. Fig. 4 must be viewed with some caution, however. The very high basicity of slag II and the high desulphurization rate imply that some significant desulphurization must have occurred even before the slag was judged to be molten. Accordingly, a better "zero time" might be the time of the initial addition of the mixed cold slag (as oxide components). From "start of cold slag addition" to the first sample for the heats of Fig. 4 the times are: heat 73, 95 min; heat 79, 95 min; heat 86, 140 min; and heat 87, 165 min. Even on this basis

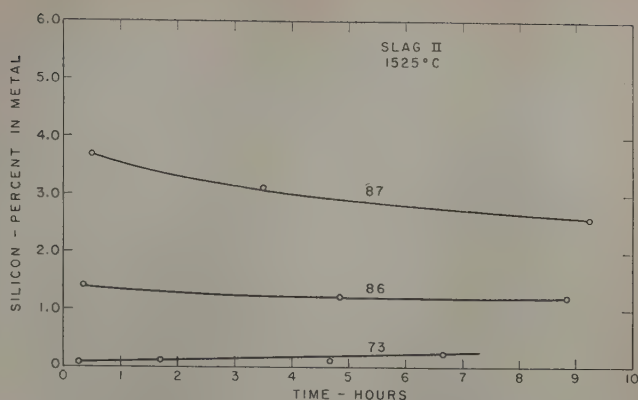


Fig. 2—Change in silicon content of metal with time for slag II at 1525°C.

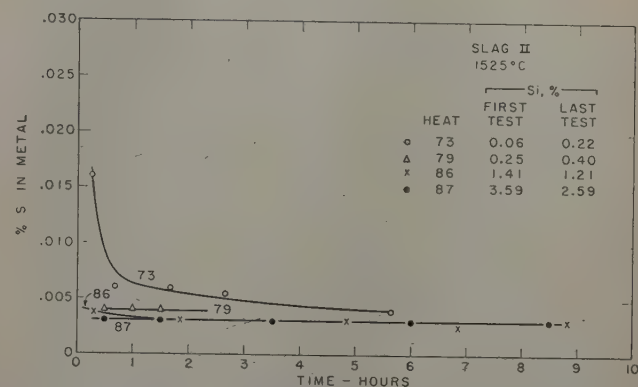


Fig. 4—Decrease in sulphur in metal with time for slag II at 1525°C for heats of different initial silicon content.

there is, however, a significant improvement in desulphurization rate as the silicon in the charge increases. There also appears to be a slight improvement in the final sulphur with increased silicon content of the metal.

**Distribution of Silicon Between Slag and Metal:** There are no experimental data in the literature on the equilibrium between silicon in pig iron and silica in the slag. This equilibrium is expected to be strongly affected by temperature and by slag basicity. The latter effect is demonstrated in Figs. 1 and 2. Under the more basic slag II the equilibrium silicon content is in the vicinity of 1.2 pct, while with the more acid slag IV it is well above 4 pct. In a qualitative way the data of Hatch and Chipman and of Grant, Kalling, and Chipman show the same effect. Further research is clearly needed before quantitative conclusions regarding this equilibrium can be drawn.

### Summary

The rate of removal of sulphur from molten pig iron is affected by the silicon content of the iron. The results are interpreted as showing that silica in the slag is a sufficiently good oxidizing agent to interfere with the principal desulphurizing reactions. When sufficient silicon is present to prevent further reduction of silica the transfer of sulphur from metal to slag is extremely rapid.

The distribution of silicon between slag and metal is an important factor in desulphurization and requires further study.

### Acknowledgments

The authors wish to express their appreciation to the American Iron and Steel Institute for support of the research.

Table II. Silicon Additions

| Heat | Slag No. | Approximate Addition |
|------|----------|----------------------|
| 82   | IV       | 8 g Si (2.0 pct)     |
| 83   | IV       | 14 g Si (3.4 pct)    |
| 84   | IV       | 19 g Si (4.5 pct)    |
| 86   | II       | 8 g Si (2.0 pct)     |
| 87   | II       | 19 g Si (4.5 pct)    |

# Desulphurizing Action of Titanium in Steels

by W. P. Fishel, William P. Roe, and James F. Ellis

This paper reports the distribution of sulphur between iron and titanium in Fe-Ti-S alloys and in Fe-Ti-C-S alloys. The compound TiS was found, which exists as a separate phase at temperatures below 1200°C. Titanium in steels reacts with sulphur in preference to carbon.

THE general relationship between sulphides and oxides suggests that titanium should form a sulphide having properties similar to those of titanium oxide. Specifically, titanium should form a sulphide having a high melting point, indicating a stable compound of low solubility in iron. In order for titanium to function as a desulphurizer or sulphur-fixing agent, it must form a stable sulphide. In order for titanium to be useful in steels as a sulphur-fixing agent, it must react with sulphur in preference to carbon; and to prevent red shortness, the sulphide formed must have solubility characteristics such that grain-boundary precipitation of a low melting phase be prevented. The terms desulphurizer and sulphur-fixing agent when used in this paper mean that titanium effectively ties up the sulphur as a stable sulphide of titanium and prevents the formation of FeS.

The partition of sulphur between iron and titanium was studied first in a series of Fe-Ti-S alloys with carbon absent, and then in similar alloys with carbon present.

It has been established<sup>1,2</sup> that titanium forms in Fe-Ti-S alloys a sulphide of undetermined composition which can be identified microscopically, and that the titanium-sulphur compound does not respond to sulphur printing. It has been suggested<sup>3</sup> that titanium acts as a sulphur-fixing agent, although little proof has been given. A report<sup>4</sup> of The Advisory Committee on Metals and Minerals summarizes the existing knowledge concerning substitutes for manganese in steels.

## Distribution of Sulphur Between Iron and Titanium with Carbon Absent

The alloys for this investigation were made by melting Armco iron, metallic titanium, and iron sulphide in alundum crucibles in an induction furnace. The titanium was added after the other ingredients had melted. In these alloys it is recognized that some TiO<sub>2</sub> is present, since the melts were made in the air and since no other deoxidizing agent was used; therefore, some of the titanium was not available for union with sulphur. Thirteen ingots were made. Ingots 2 to 8 were cast in baked-sand molds; ingots 12 and 13 were cast in metal molds;

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and ingot 9 was allowed to cool in the crucible in which it was melted. All ingots were annealed at 900°C for 3 hr and were cooled slowly in the furnace. Subsequent information indicates that this anneal had no effect upon the titanium sulphide particle size, since the sulphide does not go into solution at this temperature. The ingots as-cast were approximately 8 in. long and 3/4 in. diam. The compositions of the eight ingots and the results of the partition of sulphur are recorded in Table I.

Total titanium and total sulphur were determined by standard gravimetric methods. Sulphur, as iron sulphide, was determined by the evolution method. Boiling HCl (1:4) liberates the sulphur from iron sulphide, but leaves the titanium sulphide practically undecomposed. A complete separation of titanium sulphide and iron sulphide cannot be made by digesting these compounds in dilute HCl since titanium sulphide was found to dissolve slowly. The amount of titanium sulphide decomposed will depend upon the time in contact with the acid and upon the particle size of the sulphide. The point

Table I—Partition of Sulphur between Titanium and Iron

| Alloy | Total Ti, Pct | Total S, Pct | Ratio Ti:S | S Soluble in HCl, Pct (S as FeS) | S Insoluble in HCl, Pct (S as TiS) | Total S as TiS, Pct |
|-------|---------------|--------------|------------|----------------------------------|------------------------------------|---------------------|
| 2     | 0.385         | 0.504        | 0.77       | 0.458                            | 0.025                              | 5.2                 |
|       | 0.395         | 0.504        |            | 0.456                            | 0.026                              |                     |
|       | 0.390         | 0.504        |            | 0.457                            | 0.026                              |                     |
| 4     | 0.211         | 0.182        | 1.13       | 0.158                            | 0.011                              | 7.0                 |
|       | 0.209         | 0.190        |            | 0.162                            | 0.014                              |                     |
|       | 0.210         | 0.186        |            | 0.160                            | 0.013                              |                     |
| 5     | 0.468         | 0.207        | 2.27       | 0.163                            | 0.031                              | 15.0                |
|       | 0.458         | 0.201        |            | 0.164                            | 0.029                              |                     |
|       | 0.463         | 0.204        |            | 0.164                            | 0.030                              |                     |
| 6     | 0.515         | 0.189        | 2.75       | 0.135                            | 0.039                              | 22.2                |
|       | 0.511         | 0.187        |            | 0.138                            | 0.041                              |                     |
|       | 0.513         | 0.188        |            | 0.137                            | 0.040                              |                     |
| 8     | 0.368         | 0.122        | 2.86       | 0.012                            | 0.080                              | 62.0                |
|       | 0.372         | 0.135        |            | 0.013                            | 0.079                              |                     |
|       | 0.370         | 0.129        |            | 0.013                            | 0.080                              |                     |
| 9     | 0.700         | 0.329        | 2.15       | 0.011                            | 0.313                              | 95.5                |
|       | 0.699         | 0.320        |            | 0.011                            | 0.307                              |                     |
|       | 0.700         | 0.325        |            | 0.011                            | 0.310                              |                     |
| 12    | 0.240         | 0.234        | 1.04       | 0.092                            | By difference                      | 56.7                |
|       | 0.251         | 0.240        |            | 0.114                            |                                    |                     |
|       | 0.246         | 0.237        |            | 0.103                            | 0.134                              |                     |
| 13    | 0.154         | 0.315        | 0.52       | 0.133                            | By difference                      | 54.5                |
|       | 0.161         | 0.295        |            | 0.144                            |                                    |                     |
|       | 0.158         | 0.305        |            | 0.139                            | 0.166                              |                     |



involved is one of reaction or solution rates. Therefore, the figures representing sulphur as FeS in Table I are probably high, and those for sulphur as TiS are correspondingly low. The sulphur not liberated by HCl in the evolution flask was determined gravimetrically. This was considered to be titanium sulphide, which in this paper is represented by the formula TiS.

The percentages of sulphur in these alloys are much higher than would be found in commercial steels. They were made so intentionally in the interest of better separations. The ratio of titanium to sulphur as well as the amounts of titanium and sulphur in these alloys cover wide ranges. In alloys 2, 4, 5, 6, and 8, which were cast in sand molds, there is a gradual increase in the ratio of titanium to sulphur from 0.77 to 2.68. There is also an increase in the amount of total sulphur combined with titanium as the Ti:S ratio increases. The rapid cooling given these alloys produced finely divided particles of titanium sulphide. These small sulphide particles suffered more loss by solution during the evolution analysis with HCl than did the larger particles of alloy 9. The values given for sulphur as TiS could be too low if the samples were digested for a very long time, or too high if not digested long enough so that some FeS was left undecomposed. Considering the methods used in these analyses, it is believed that the values given for sulphur as TiS in most cases are low.

Alloy 9 was cooled slowly from the melt and was found to contain large particles of titanium sulphide. In this alloy 95.5 pct of the total sulphur was present as TiS, although the ratio of Ti:S was only 2.15. In Fig. 1 the micrographs of alloy 9 show large sulphide particles.

Alloys 12 and 13 were cast in metal molds. They had low ratios of Ti:S, yet they showed a rather high percentage of sulphur as TiS. This is probably due to better melting procedures that resulted in less oxidation of the titanium and hence left a higher percentage of titanium to react with sulphur.

From the data presented in Table I, it is evident that titanium reacts with sulphur and that the distribution of sulphur between titanium and iron varies with the amounts of titanium and sulphur present. The ability of titanium to tie up sulphur becomes more pronounced than the above data indicate, when it is remembered that part of the titanium in these alloys has united with oxygen and is not available for union with sulphur.

### Composition of Titanium Sulphide

In order to determine the composition of the sulphide formed, residues were prepared from alloy 9. This alloy was carbon-free and contained large sulphide particles. Approximately 300 g of turnings were taken from this alloy and were treated with 1:4 HCl at room temperature in a flask from which air was excluded. After all visible action had ceased, the acid was siphoned off and fresh acid added. This process was continued for six weeks. At this time no noticeable action accompanied the addition of fresh acid. A finely-divided, black residue remained which was washed several times with distilled water and allowed to settle. The same procedure then was carried out with absolute alcohol. The alcohol suspension of the residue was centrifuged; only the heavier portion of the residue was collected. At this point the residue appeared bronze in color. The alcohol was poured off, and the last



Fig. 1—Micrograph of Alloy 9.  
Upper—Fe-Ti-S, unetched. Particles of titanium sulphide and boundary segregation. X160.  
Lower—Unetched. Particles of titanium sulphide. X650.

traces were removed by repeated ether treatments. The ether was removed by centrifuging and evaporation; a finely-divided, black powder remained. This residue was nonmagnetic, and appeared stable in air.

This residue was analyzed and gave the following results: Ti, 59.2 pct, 59.2 pct; and S, 18.2 pct, 18.1 pct.

Approximately 20 pct of the total is unaccounted for. The amount missing is about equal to the sulphur present. The most obvious explanation is that the residue is a mixture of about equal parts of TiS and  $TiO_2$ . Any mixture of TiS and  $TiO_2$  when ignited to  $TiO_2$  would not change weight, since one sulphur (atomic wt 32.07) is replaced by two oxygens (atomic wt 16.00). This would not be true for any other sulphide of titanium or for a nitride or a carbide.

A sample of the residue was ignited to constant weight. Sulphur dioxide was evolved and a white powder resulted. The weights were as follows: weight of residue, 0.0714 g; weight after ignition, 0.0717 g; and pct Ti in the residue, 60.2 pct. The ignited residue is  $TiO_2$ . This is considered proof that the sulphide present in the alloy has the formula TiS. The slight gain in weight which occurred could be attributed to some TiN being converted to  $TiO_2$ .

**Solubility:** In order to determine the temperature at which the sulphide formed or precipitated from solid solution, which should be near the temperature at which it dissolved on heating, several heating and quenching tests were made.

Four pieces of alloy 9 were taken. One sample was held for 2 hr at each temperature listed in

Table II—Temperature and Hardness Tests for Alloy 9

| Sample Temperature, °C | Hardness before Quenching, Rockwell E | Hardness after Quenching, Rockwell E |
|------------------------|---------------------------------------|--------------------------------------|
| 1000                   | 48                                    | 50                                   |
| 1100                   | 48                                    | 90                                   |
| 1200                   | 48                                    | 93                                   |
| 1250                   | 48                                    | 93                                   |

Table II and then quenched in water. Evidently the TiS did not dissolve at 1000°C, but did dissolve to some extent at 1100°C. This conclusion is confirmed by the microstructure. By a comparison of the structure before and after annealing, it was observed that the large sulphide particles had broken down to some extent at the higher temperatures into smaller ones, and that some grain-boundary precipitation had taken place.

#### Distribution of Sulphur between Titanium and Iron with Carbon Present

For this study five alloys were made exactly as before with the exception that carbon was added as lump graphite. The carbon was added immediately after the iron was molten and before the addition of titanium. The addition of carbon produced sounder ingots due to the deoxidation of the metal, this in turn allowed for less oxidation of the alloying element so that titanium could exert its full effect as a desulphurizing agent. The melts were poured into metal molds and were annealed at 900°C.

The alloys were analyzed for total titanium, total sulphur, total carbon, sulphur as FeS, sulphur as TiS, and carbon as TiC. Since TiC is insoluble in HCl, a good approximation of the amount of titanium united with carbon may be had by dissolving the steel in dilute HCl, filtering the insoluble residue in a combustion thimble, and igniting to CO<sub>2</sub>. The residue from HCl contains all of the TiC present in the steel and some free carbon resulting

Table III—Compounds Present in Iron-Titanium-Sulphur-Carbon Alloys

| Alloy | Total Ti (I)   | Total S (II)   | Ratio Ti:S (III) | Total C (IV)   | Ratio Ti:C (V) | C Insoluble in HCl, Pct (C as TiC)* (VI) | S Soluble in HCl, Pct (S as FeS) (VII) | S Insoluble in HCl, Pct (S as TiS by Difference) (VIII) | Total S as TiS, Pct (IX) |
|-------|----------------|----------------|------------------|----------------|----------------|------------------------------------------|----------------------------------------|---------------------------------------------------------|--------------------------|
| A     | 0.380<br>0.392 | 0.313<br>0.357 |                  | 0.272<br>0.274 |                | 0.079<br>0.076                           | 0.128<br>0.148                         | 0.197                                                   |                          |
|       | 0.386          | 0.335          | 1.15             | 0.273          | 1.41           | 0.078                                    | 0.138                                  | 0.130                                                   | 39                       |
| B     | 0.282<br>0.282 | 0.292<br>0.279 |                  | 0.109<br>0.109 |                | 0.032<br>0.027                           | 0.085<br>0.085                         | 0.201                                                   |                          |
|       | 0.282          | 0.286          | 0.99             | 0.109          | 2.59           | 0.030                                    | 0.085                                  | 0.198†                                                  | 61                       |
| C     | 0.198<br>0.221 | 0.246<br>0.254 |                  | 0.151<br>0.143 |                | 0.024<br>0.033                           | 0.089<br>0.084                         | 0.164                                                   |                          |
|       | 0.210          | 0.250          | 0.84             | 0.147          | 1.43           | 0.028                                    | 0.086                                  | 0.182†                                                  | 74                       |
| D     | 0.281<br>0.260 | 0.221<br>0.177 |                  | 0.154<br>0.152 |                | 0.027<br>0.019                           | 0.092<br>0.092                         | 0.102                                                   |                          |
|       | 0.270          | 0.194          | 1.39             | 0.153          | 1.77           | 0.023                                    | 0.092                                  | 0.109†                                                  | 56                       |
| E     | 0.206<br>0.214 | 0.206<br>0.185 |                  | 0.358<br>0.363 |                | 0.028<br>0.034                           | 0.065<br>0.071                         | 0.128                                                   |                          |
|       | 0.210          | 0.196          | 1.07             | 0.361          | 0.58           | 0.031                                    | 0.068                                  | 0.133†                                                  | 67                       |

\* These values are too high due to free carbon from Fe<sub>3</sub>C.

† Results by analysis.

from the action of the acid upon Fe<sub>3</sub>C. The values for carbon as TiC are therefore a little higher than the true values.

Table III gives the compositions of the five alloys and the compounds found in them. There is more carbon present than is required to react with all the titanium. Despite the presence of excess carbon, the data show that a considerable amount of titanium sulphide is formed. For example, in alloy D over half the sulphur is present as titanium sulphide, even though the Ti:S ratio is only 1.39, and in spite of the presence of twice as much carbon as is needed to react with all the titanium present. Some of the values presented in Table III do not agree very well among themselves. If the amount of titanium as carbide and the amount as sulphide is calculated, the total is greater than the total titanium listed. Part of this discrepancy is due to the known high values of C as TiC, col. VI, part to the inability to make a clean separation between FeS and TiS, and the remainder to analytical errors. In spite of the inexactness of the figures presented, Table III serves to give a qualitative picture of the distribution of sulphur between titanium and iron in alloys containing carbon. In all these alloys, with the exception of alloy A, over half the total sulphur is present as HCl-insoluble titanium sulphide. Very little titanium carbide is present. The values for C as TiC, col. VI, multiplied by 4 gives the titanium as TiC. It will be noted that the Ti:S ratios in these alloys are below 1.5, the ratio for TiS; hence there is insufficient titanium present to react with all the sulphur. At this stage of the research the identity of the titanium sulphide was not known; otherwise, alloys with higher ratios would have been used. Later work by another investigator shows that if the Ti:S ratio is above 2, nearly all the sulphur is present as TiS.<sup>5</sup>

These alloys were examined microscopically. All contained pearlite and particles of titanium sulphide.

From the above it would appear that titanium in steels reacts with sulphur in preference to carbon, and that titanium tends to tie up sulphur as a sulphide, thus inhibiting the formation of iron sulphide.

One ingot containing 0.5 pct C, 0.05 pct S, 0.15 pct Ti, but no manganese was hot rolled to a thin strip. Several ingots of similar compositions were hot forged. The hot working properties were normal.

#### Conclusions

1—It has been shown that titanium will react with sulphur in steels containing carbon to form TiS, insoluble in  $\gamma$  iron below 1000°C; and that titanium reacts with sulphur in preference to carbon.

2—Titanium can replace manganese as a sulphur-getter in steels.

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# Grain Structure of Aluminum-Killed, Low Carbon Steel Sheets

by R. L. Solter and C. W. Beattie

**A**LUMINUM-KILLED, low carbon steel sheets are used extensively for severe deep drawing and other difficult forming operations. They usually, but not always, have a characteristic grain structure in which the grains are elongated both in the lengthwise and in the transverse direction. As described by Burns and McCabe,<sup>1</sup> a typical grain in the plane of the sheet has its two axes in that plane from  $1\frac{1}{2}$  to 4 times as long as the axis normal to the plane of the sheet. Rickett, Kalin, and MacKenzie<sup>2</sup> have also reported on the recrystallization behavior of such steel. The contrast in grain structures of fully processed sheets of aluminum-killed and rimmed steel is illustrated by Figs. 1 and 2. The elongated grain structure of the aluminum-killed sheet is not developed on all heats or lots of this metal, and studies of the factors controlling and influencing its formation are reported in this paper.

Jeffries and Archer<sup>3</sup> state that unstrained grains are normally equiaxed, but exceptions are common. For example, if a metal containing a material mechanically obstructing grain growth is subjected to considerable working followed by thorough annealing, it may exhibit grains consistently elongated in the direction of working. Our experiments demonstrate that aluminum-killed, low carbon steel is such a metal, and that the substance mechanically obstructing grain growth is aluminum nitride. The effectiveness of aluminum nitride in inhibiting grain growth has been found to be influenced by the degree of cold reduction, the rate of heating in annealing, the thermal history of the sample before cold reduction, and the residual aluminum content. A correlation between grain shape and austenitic grain coarsening temperature also was indicated and additional experiments demonstrated that aluminum nitride is also the principal cause for the fine grain characteristic of aluminum-killed steels.

## Manufacture

In conventional practice, aluminum-killed sheet steel is manufactured from a low carbon steel containing approximately 0.02 to 0.07 pct residual (HCl-soluble) Al. With the exception of certain samples containing greater or lesser amounts of aluminum, the steels used in these investigations were within the following composition range: C, 0.03 to 0.06 pct; Mn, 0.28 to 0.38; S, 0.017 to 0.032; Al, 0.03 to 0.06; P, <0.01; and Si, <0.01.

Properly heated ingots are rolled to slabs about 4 in. thick. After surface conditioning, the slabs are reheated to about 2300°F and hot rolled continuously to strip about 1/10 in. thick. The strip rolling

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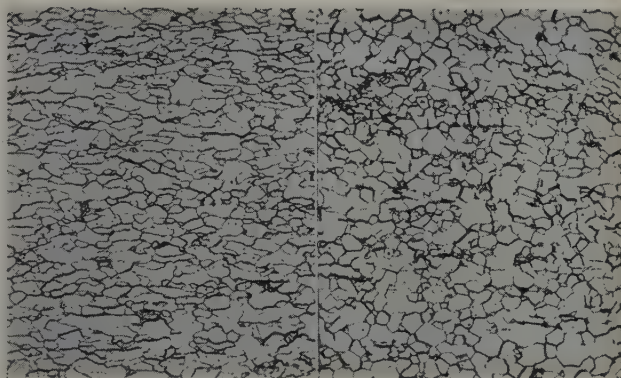


Fig. 1—Grain structure of aluminum-killed drawing sheet. X100

Fig. 2—Grain structure of rimmed steel drawing sheet. X100.

is completed at a temperature of 1550°F or higher, and the strip is coiled, usually at a temperature near the lower critical transformation. After cooling, the strip is pickled to remove oxide, cold reduced 40 to 70 pct to final thickness, then annealed to 1250° to 1350°F in 20 to 80 ton charges, the size of which results in slow heating and cooling rates.

## Effect of Cold Reduction

According to Sachs and Van Horn,<sup>4</sup> the deformations of the individual grains in rolling are similar to those of the total volume. Thus individual grains would elongate in rolling according to the amount of cold reduction imposed. This is true theoretically, but as cold reduction increases the individual grains tend to fragment, and measured grain elongations become less than theoretical. The amount of grain elongation may be described by a numerical rating based on grain counts made by the intercept method. Specimens are polished normal to the plane of the sheet, with the polished surface extending parallel to the rolling direction.

After etching, grain intercepts are counted along a 50 mm line on a micrograph of suitable magnification. In random locations parallel to the plane of the sample 20 counts are made and 20 are made in the thickness direction of the sample. The average count in the thickness direction divided by the average count parallel to the plane of the sample gives a numerical rating of the grain shape called grain elongation. For example, a grain elongation of 2.00 means that the average grain is twice as long as it is thick. The average of both counts may be converted to grains per sq mm by a nomograph relating intercept counts and grain count. By the same procedure the grain elongation in the plane of the sheet but transverse to the rolling direction may be determined, using transverse metallographic samples.

A comparison of theoretical and measured grain elongation was obtained on an aluminum-killed

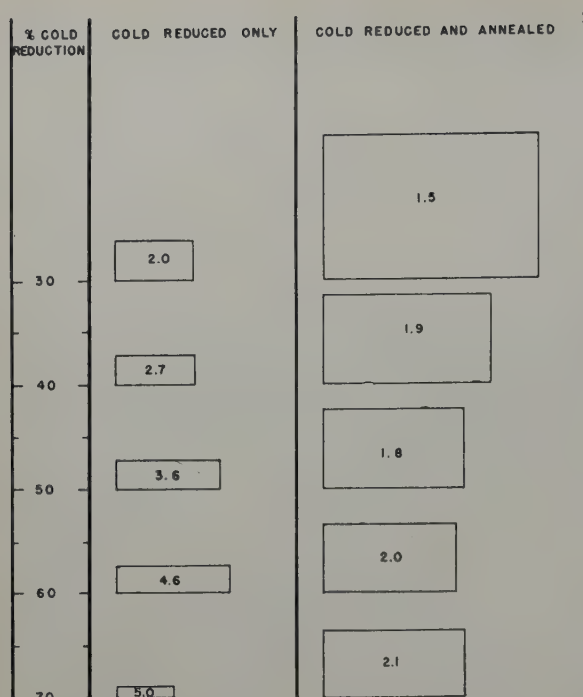


Fig. 3—Relative grain dimensions and shape in the plane of a material cold reduced only and of a duplicate material cold reduced and annealed at 1340°F. Samples were polished parallel to the rolling direction. Numbers within rectangles are grain elongation rating.

steel that had been hot rolled and then cold reduced various amounts. This steel contained 0.046 pct C, 0.33 pct Mn, 0.026 pct S, and 0.034 pct residual Al. Cold-reduced specimens were annealed at 1340°F and grain elongations were measured on the annealed materials. This comparison is given in Table I. Measurements were impossible on specimens cold reduced 80 and 90 pct because of the extreme distortion, but it seems probable that grain elongations were considerably less than the theoretical value.

Values in Table I show that, as cold reduction increased, fragmentation of individual grains occurred and the measured elongation was considerably less than was calculated. The amount of grain elongation measured after annealing was less than after cold reduction, consequently the elongation imposed by cold work was only partially retained after annealing, indicating that any mechanical obstruction to grain growth was not completely effective. Relative grain sizes and shapes of an individual material in the cold-reduced and the cold-reduced and annealed condition are shown by appropriately dimensioned rectangles in Fig. 3. The larger grain size of annealed specimens of this material is further evidence that mechanical obstruction did not completely inhibit grain growth.

This illustration is an individual case representative of one material. Measurements of 14 other samples gave a diversity of results. No two reacted

Table I. Comparison of Grain Elongations Calculated for Cold-Reduced Specimens with Grain Elongations Measured on Cold-Reduced Only and Cold-Reduced and Annealed Specimens

| Cold Reduction, Pct | Calculated | Measured on Cold-Reduced Specimens | Measured on Annealed Specimens |
|---------------------|------------|------------------------------------|--------------------------------|
| 30                  | 2.0        | 2.0                                | 1.5                            |
| 40                  | 2.8        | 2.7                                | 1.9                            |
| 50                  | 4.0        | 3.6                                | 1.8                            |
| 60                  | 6.2        | 4.6                                | 2.0                            |
| 70                  | 11.2       | 5.0                                | 2.1                            |
| 80                  | 25.1       |                                    | 2.6                            |
| 90                  | 100.0      |                                    | 3.0                            |

exactly alike to the influence of cold reduction. Such inconsistency indicated that factors other than the amount of cold reduction influenced grain size and shape. However, the average values of grain elongation and grain count show that a definite relationship exists with variations in cold reduction, as illustrated in Fig. 4. Both grain elongation and grain count increased with increasing cold reduction with a noticeable change in rate of increase above 60 pct. Grain elongation and grain size also appear to be related when compared at a given cold reduction. A group of 124 materials was cold reduced 60 pct and annealed at 1340°F. Grain counts and grain elongations were determined. These data were listed in order of decreasing grain elongations and grouped in ten approximately equal groups. The average grain elongation and grain count was determined for each group and plotted in Fig. 5. This curve demonstrates that for a given amount of cold reduction a sample with a larger grain count was likely to have less grain elongation than one with a smaller grain count. Thus, the final grain structure becomes finer and more elongated as cold reduction increases, but the amount of grain elongation developed by a given amount of cold reduction is more if the grain size is larger.

### Effect of Variations in Heating to the Annealing Temperature

Three hot-rolled strip materials were secured, each from a different heat, as given in Table II. These materials were cold reduced 60 pct and annealed with two variations in heating rate. Variation 1 consisted of heating the samples to 1340°F in ½ hr. Variation 2 consisted of heating the samples

Table II. Composition of Materials, Pct

| Element     | Material 1 | Material 2 | Material 3 |
|-------------|------------|------------|------------|
| C           | 0.041      | 0.040      | 0.039      |
| Mn          | 0.33       | 0.26       | 0.32       |
| S           | 0.019      | 0.020      | 0.020      |
| Residual Al | 0.043      | 0.038      | 0.042      |

to 1340°F in 22 hr using a uniform rate of 25°F per hr above 800°F. In both instances samples were held at temperature 4 hr and cooled 25°F per hr to about 500°F before removing from the furnace. Grain elongation and grain counts resulting from these treatments are shown in Table III. Grain structures of Material 2 are shown in Fig. 6. These data show that fast heating resulted in a finer grain with less elongation than slow heating.

The same three materials were given a 2 hr heat treatment at temperatures of 300° to 1100°F prior to annealing with heating Variation 1. Heating for 2 hr at 700° to 1100°F caused the final grain structure to be coarser and more elongated than would normally have been expected from heating Variation 1. This is illustrated in Fig. 7.

### Determination of Aluminum Nitride

These and other studies led to the belief that the observed recrystallization behavior of aluminum-killed steel is influenced principally by the precipitation of a constituent during the heating portion of the annealing cycle. It was long suspected that this constituent was aluminum nitride. H. F. Beeghly<sup>6</sup> recently reported a sound and reproducible method for determining this compound, and demonstrated that the amount present varied with the heat treatment received by the sample before analysis. Hot-rolled, aluminum-killed steel samples were shown to contain different amounts of nitrogen as alu-



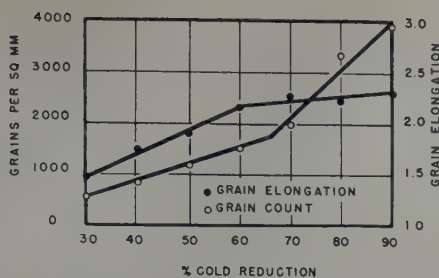


Fig. 4—Relationship of grain count and grain elongation of samples cold reduced and annealed at 1340°F.

minum nitride if reheated 1 hr at various temperatures. His data are plotted in Fig. 8. As hot-rolled, the amount of nitrogen combined as aluminum nitride is low, but as the annealing temperature increased, the amount increased to a maximum in a temperature range from about 1300° to 1800°F. At temperatures above 1800°F, the amount decreased until at about 2350°F no more was present than in the original hot-rolled bar. This indicates that aluminum nitride is held in supersaturated solution in hot-rolled samples. If the samples are reheated the aluminum nitride precipitates up to a maximum amount at 1300° to 1800°F and at higher temperatures it redissolves.

This precipitation and re-solution of aluminum nitride is believed to be responsible for the behavior of aluminum-killed steels both with respect to the grain shape of the cold-reduced and annealed sheets and to the austenitic grain refining characteristic of such steels, and has been demonstrated by the following experimental procedures.

#### Effect of Thermal History before Cold Reduction

In considering the effect of thermal history on grain shape it should be understood that the grain shape referred to in the following discussion is that of the final cold-reduced and annealed product, even though the heat treatments described may have been performed before cold reduction and final annealing. Twelve samples of hot-rolled strip with the normal chemistry range were secured and reheated; one group to 1800°F and air cooled, a duplicate group to 1800°F and furnace cooled, a third group to 2100°F and air cooled, and a fourth group to 2100°F and furnace cooled. Following heat treatment the samples were cold reduced 60 pct and annealed at 1340°F. After annealing the structures were as shown in Fig. 9. All had equiaxed grain structures except those heated to 2100°F and air cooled before cold reduction. This group had the elongated grain

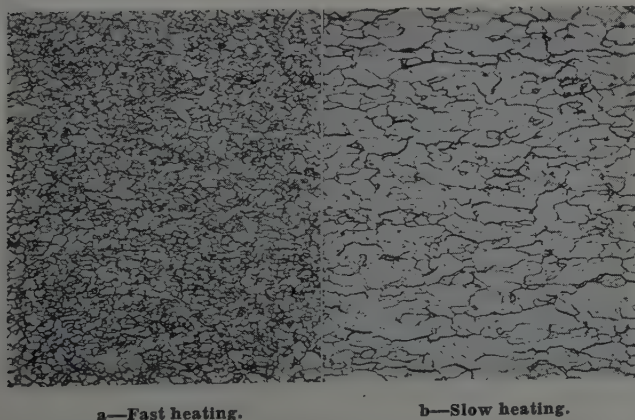


Fig. 6—Effect of heating rate during annealing of cold-reduced samples. X100.

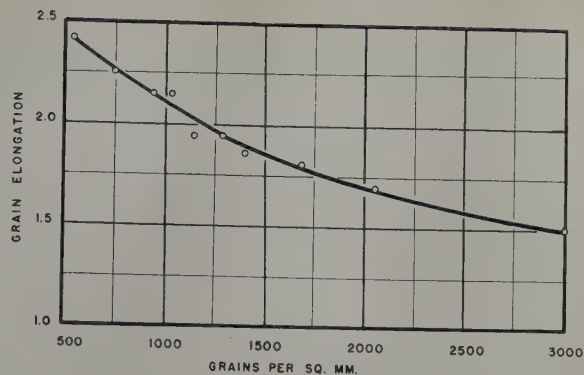


Fig. 5—Relationship of grain elongation to grain count of samples cold reduced 60 pct and annealed at 1340°F.

shape as would be expected for this type of steel. The grain structures of samples heated to 2100°F were coarse as compared to those heated to 1800°F, showing that the coarsening temperature was reached or exceeded by the 2100°F treatment.

Heating to 2100°F and air cooling is believed to have caused a re-solution of aluminum nitride and a retention of the compound in supersaturated solid solution. In the final anneal after cold reduction, the aluminum nitride precipitated in the normal manner and resulted in an elongated grain structure. In the other heat treatments, precipitation of aluminum nitride occurred in the strip before cold reduction. This behavior was demonstrated in a slightly different manner by heat treatments performed on hot-rolled strip. Five different hot-rolled strip materials were used. The nitrogen content as aluminum nitride and the total nitrogen content (includes iron nitride, etc.) were determined on the hot-rolled

Table III. Grain Count and Elongation of Materials Heated Slow or Fast to 1340°F

| Vari-<br>ation | Approx.<br>Heat-Up<br>Time,<br>Hr | Material 1             |        | Material 2             |        | Material 3             |        |
|----------------|-----------------------------------|------------------------|--------|------------------------|--------|------------------------|--------|
|                |                                   | Grains<br>per Sq<br>Mm | Elong. | Grains<br>per Sq<br>Mm | Elong. | Grains<br>per Sq<br>Mm | Elong. |
| 1 Fast         | ½                                 | 5800                   | 1.6    | 6300                   | 1.3    | 8000                   | 1.3    |
| 2 Slow         | 22                                | 2400                   | 1.8    | 950                    | 2.6    | 2400                   | 1.9    |

strip: 1—as hot rolled, 2—as hot rolled, cold reduced, and annealed at 1340°F, 3—as air cooled from 2100°F, and 4—as furnace cooled from 2100°F. Nitrogen contents as aluminum nitride were determined by the Beeghly method<sup>6</sup> and total nitrogen contents by another Beeghly method.<sup>6</sup> The results are listed in Table IV.

The nitrogen determinations of Group 1 for the “as hot-rolled” condition show the low nitrogen as

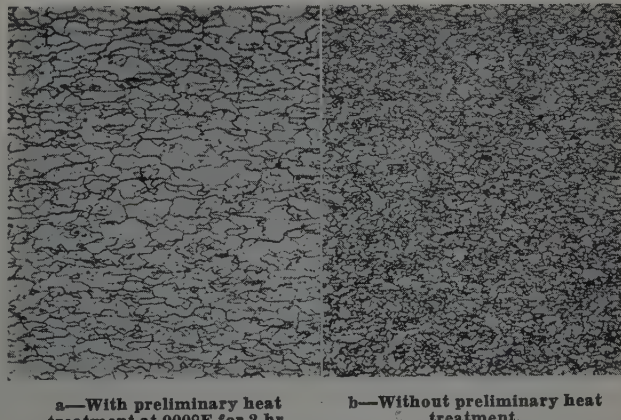


Fig. 7—Grain structures resulting from annealing samples with fast heating. X100.



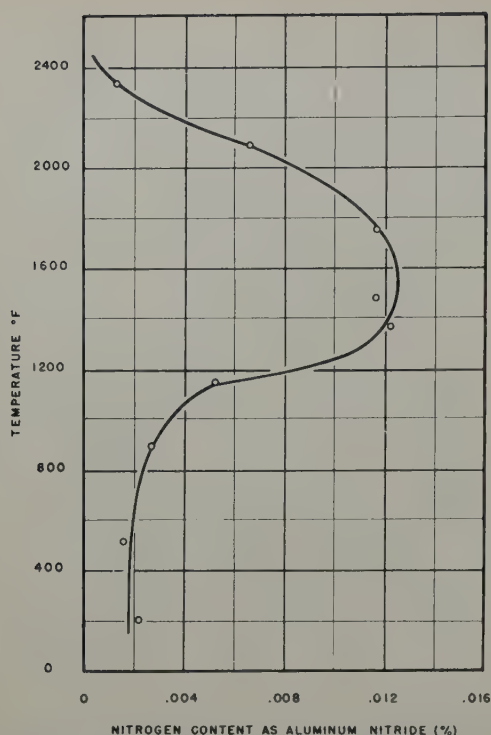


Fig. 8—Aluminum-killed steel hot rolled and reheated 1 hr at various temperatures (after Beeghly).

aluminum-nitride values which are characteristic of rapid cooling from above the critical temperature range. Group 2 for the cold-reduced and annealed condition shows that practically all of the nitrogen present has precipitated as aluminum-nitride during annealing after cold reduction. Group 3 shows that air cooling from above the coarsening temperature results in even less nitrogen as aluminum-nitride than in the hot-rolled condition. On the other hand, furnace cooling from above the coarsening temperature, Group 4, resulted in considerable pick-up of total nitrogen from the air atmosphere and the precipitation of most of it as aluminum-nitride. Samples were wrapped in soft steel sheets to minimize this but aluminum-bearing steels display a great affinity for nitrogen.

In another experiment two specimens of roughing mill stock  $\frac{3}{4}$  in. thick were heated to 2100°F; one was air cooled to room temperature, the other was furnace cooled. Both were cold reduced 45 pct and annealed at 1340°F. This gave two kinds of material; the air-cooled sample in which precipitation took place during annealing after cold reduction and the furnace-cooled sample in which precipitation occurred before cold reduction. Charpy impact speci-

mens cut parallel to the rolling direction and notched at one surface were broken at a series of temperatures with results listed in Table V. Material with the elongated grain shape had considerably less impact resistance than the same material with equiaxed grain shape. Precipitation of aluminum nitride at the boundaries of the elongated grains in the air-cooled sample, creating planes of weakness, could account for the reduced impact resistance. An equal amount of precipitate in the boundaries of the equiaxed grains of the furnace-cooled sample would not have the same effect on the impact resistance.

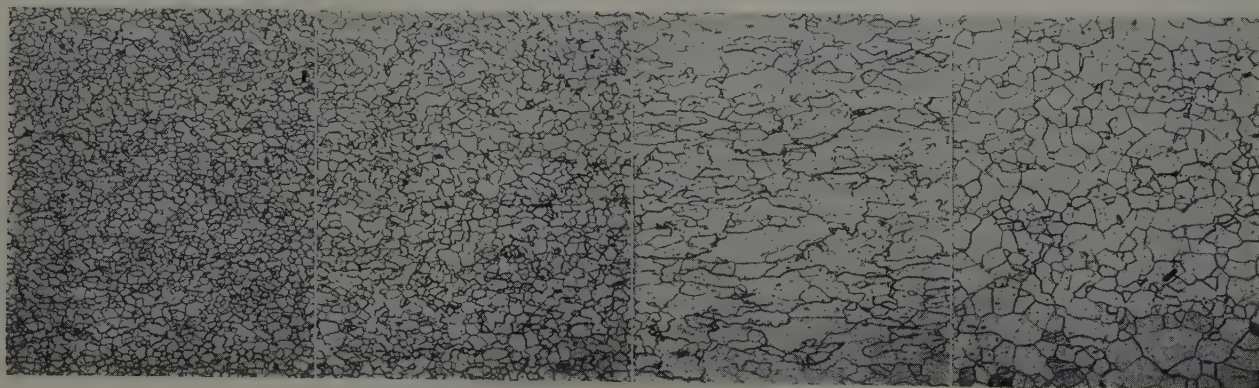
#### Effect of Cooling Rate and Heat Treatment

The effect of retarding the cooling rate after finishing the hot-rolled strip at 1550°F was studied, together with the effect of reheating such strip after air cooling or coil cooling. Strip hot rolled and held, or reheated and held at constant temperature for a certain minimum time was no longer capable of producing the elongated grain shape after cold reduction and box annealing, but yielded equiaxed grain structures. The higher the holding temperature, the less was the time required to effect the change. The minimum times required to change grain shape from elongated to equiaxed as determined on one lot of material are shown in Fig. 10. The reheating time was least for mill-rolled and coiled strip, indicating that precipitation was partially completed during coil cooling.

The effect of reheating hot-rolled strip on the nitrogen content as aluminum nitride was determined on the same five materials shown in Table IV. These materials were subjected to reheating times of 30, 60, and 100 min at 1250°F. Results of chemical analyses before cold reduction and annealing and the microstructure after cold reduction and annealing are listed in Table VI. Tests on hot-rolled only (no reheating) samples are included for comparison. The data illustrate progressive precipitation of aluminum nitride with increase in holding time. It appears that after a sufficient length of time the amount of aluminum nitride remaining in solid solution was no longer influential in obstructing development of equiaxed grains after cold reduction and annealing.

#### Grain Shape Related to Grain Coarsening Temperature

Two groups of six samples each were selected on the basis of their cold-reduced and annealed grain structure. The Group 1 samples had a grain size of A.S.T.M. 6 and grain elongations varying from 2.4 to 3.1. The Group 2 samples had a grain size of A.S.T.M. 8 and grain elongations of 1.3 to 2.0. Both groups were within the following composition



a—1800°F and air cooled.

b—1800°F and furnace cooled.

c—2100°F and air cooled.

d—2100°F and furnace cooled.

Fig. 9—Grain structures of cold-reduced annealed samples heated before cold reduction.



Table IV. Effect of Heat Treatment of Hot-Rolled Strip on the Nitrogen Content as Aluminum Nitride as Compared to the Total Nitrogen Content

| Material | Chemical Composition, Pct |      |       |                | (1)<br>As Hot-Rolled, Pct |        | (2)<br>Cold-Reduced and<br>Annealed, 1340°F, Pct |        | (3)<br>Air-Cooled from<br>2100°F, Pct |        | (4)<br>Furnace-Cooled<br>from 2100°F, Pct |        |
|----------|---------------------------|------|-------|----------------|---------------------------|--------|--------------------------------------------------|--------|---------------------------------------|--------|-------------------------------------------|--------|
|          | C                         | Mn   | S     | Residual<br>Al | Total N                   | As AlN | Total N                                          | As AlN | Total N                               | As AlN | Total N                                   | As AlN |
| 1        | 0.033                     | 0.33 | 0.021 | 0.038          | 0.0042                    | 0.0003 | 0.0041                                           | 0.0034 | 0.0053                                | 0.0002 | 0.014                                     | 0.009  |
| 2        | 0.042                     | 0.33 | 0.025 | 0.044          | 0.0056                    | 0.0007 | 0.0058                                           | 0.0051 | 0.0062                                | 0.0006 | 0.016                                     | 0.014  |
| 3        | 0.047                     | 0.32 | 0.020 | 0.065          | 0.0047                    | 0.0015 | 0.0051                                           | 0.0041 | 0.0053                                | 0.0007 | 0.017                                     | 0.015  |
| 4        | 0.044                     | 0.30 | 0.024 | 0.059          | 0.0045                    | 0.0003 | 0.0050                                           | 0.0043 | 0.0043                                | 0.0003 | 0.021                                     | 0.016  |
| 5        | 0.042                     | 0.33 | 0.020 | 0.043          | 0.0053                    | 0.0007 | 0.0056                                           | 0.0051 | 0.0046                                | 0.0002 | 0.016                                     | 0.014  |

ranges: 0.031 to 0.057 pct C, 0.29 to 0.38 pct Mn, 0.017 to 0.028 pct S, and 0.037 to 0.061 pct residual (HCl soluble) Al.

When samples of the hot-rolled strip from which the 12 sheet samples had been processed were heated to 1800°F for 20 min and air cooled, all were fine grained. When heated to 1950°F for 20 min and air cooled only the six Group 2 samples were uniformly fine grained. Group 1 samples had mixed grain structures containing both coarse and fine grains. After heating to 2100°F for 20 min and air cooling, all Group 1 and 2 samples were uniformly coarse grained. The samples having larger, more elongated grains in the cold-reduced and annealed condition also coarsened at a lower temperature on heating in the austenite range.

#### Nitrogen Content Related to Grain Coarsening

The relationship of nitrogen content as aluminum nitride to grain coarsening was studied using the five hot-rolled strip materials shown in Tables IV and V. These were heated to 1700°, 1800°, 1900°, 2000°, and 2100°F and air-cooled. Microstructure and nitrogen content as aluminum nitride are given in Table VII. These data show that there is a relationship between nitrogen content as aluminum nitride and grain coarsening. Aluminum-killed steels coarsen rapidly above a certain minimum temperature, unlike rimmed steels which coarsen progressively as temperature is raised above the transformation range. Coincident with the grain growth, which takes place between 1900° and 2000°F, there is a drop in nitrogen content as aluminum nitride indicating that the precipitate is redissolved, removing the obstruction to grain growth. At 2100°F the undissolved aluminum nitride is extremely low and the materials are fully coarsened.

#### Effect of Variation in Aluminum Content

Ingots from two heats of low carbon, aluminum-killed steel were alloyed to provide a range of from 0.015 to 0.20 pct residual (HCl soluble) Al. Samples of the hot-rolled strip were cold reduced 60 pct and

annealed at 1340°F. Final grain shape, residual aluminum, and nitrogen contents as aluminum nitride are shown in Table VIII. These data show that within the range 0.034 to 0.066 pct residual Al (1B, 2A, 2B, 2C) elongated grain structure resulted after cold reducing and box annealing. The behavior of samples outside this range of residual aluminum content resulted in intermediate or equiaxed grain structures. Samples 1C, 1D, and 1E had equiaxed grains. Note that the available aluminum nitride was precipitated before cold reduction, thus leaving none available to precipitate during annealing.

However, samples 2D and 2E, with final grain structures respectively intermediate and equiaxed, did not precipitate aluminum nitride before cold reduction despite their high residual aluminum content. Reasons for this behavior contrasted to that of samples 1C, 1D, and 1E are not certain, but there are two probabilities. The coiling temperature of the hot-rolled strip may have been lower on Heat 2 than Heat 1, thereby affording less chance for the AlN to come out of solution during cooling. Second, samples 2D and 2E as well as others from Heat 2 had unusually low nitrogen content as aluminum nitride after cold reduction and annealing. The small amount precipitated during annealing in the presence of the higher aluminum content may have been ineffective in controlling grain shape. Sample 1A had a low aluminum content and a normal nitrogen content as aluminum nitride. The grain structure was intermediate between elongated and equiaxed shape, indicating that too low an aluminum content also tended to make the precipitate less effective in controlling grain shape.

Thus the optimum range for producing elongated grain structures was from somewhat above 0.015 to about 0.066 pct residual Al. This range of aluminum content is also of interest in austenite grain coarsening studies because, as shown by Washburn,<sup>7</sup> the propensity for aluminum-killed steels to be fine grained is maximum within this same range and diminishes with increased aluminum. This further indicates that the two phenomena are related, be-

Table V. Grain Size, Grain Elongation, and Charpy Values\* of Air-cooled, Cold-Reduced and Annealed Vs. Furnace-Cooled, Cold-Reduced and Annealed Aluminum-Killed Steel

| Sample                                                       | A.S.T.M. Grain<br>Size | Grain<br>Elonga-<br>tion | Charpy, Ft-Lb |      |      |      |
|--------------------------------------------------------------|------------------------|--------------------------|---------------|------|------|------|
|                                                              |                        |                          | 80°F          | 50°F | 32°F | 15°F |
| Air-cooled from<br>2100°F, cold-<br>reduced and annealed     | 6                      | 1.7                      | 36            | 11   | 6    | 8    |
| Furnace-cooled<br>from 2100°F, cold-<br>reduced and annealed | 5-6                    | 1.0                      | 83            | 35   | 26   | 20   |

\* Simple beam V-notched Charpy impact test specimen as shown in Fig. 4, p. 113, A.S.M. Metals Handbook, 1948 Edition.

Table VI. Nitrogen Content as Aluminum Nitride of Five Hot-Rolled Materials Reheated at 1250°F and Grain Shape after 60 pct Cold Reduction and Annealing

| Ma-<br>terial | As<br>Hot-Rolled,<br>Pct | Reheating Time at 1250°F, Min |          |          |
|---------------|--------------------------|-------------------------------|----------|----------|
|               |                          | 30                            | 60       | 100      |
| 1             | 0.0003 E*                | 0.0012 E                      | 0.0020 X | 0.0029 R |
| 2             | 0.0007 E                 | 0.0025 E                      | 0.0040 X | 0.0040 R |
| 3             | 0.0015 X                 | 0.0036 X                      | 0.0039 R | 0.0037 R |
| 4             | 0.0003 E                 | 0.0021 E                      | 0.0033 R | 0.0035 R |
| 5             | 0.0007 E                 | 0.0012 E                      | 0.0030 X | 0.0044 R |

\* Letters indicate grain shape after cold reduction and box annealing: E = elongated; X = intermediate; R = round or equiaxed.

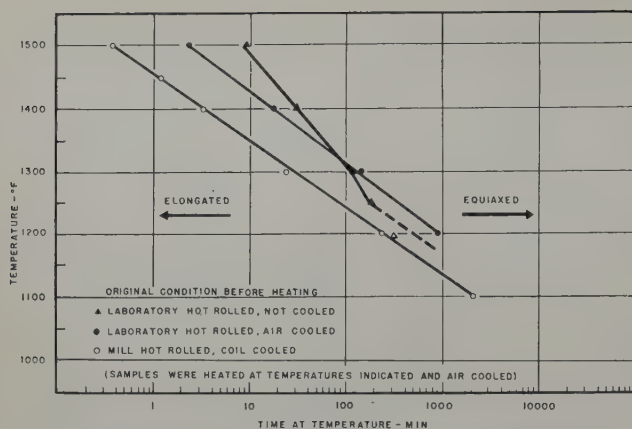


Fig. 10—Minimum time to change grain shape from elongated to equiaxed by heating hot strip before cold reduction.

cause both fine grain behavior and grain elongation characteristics diminish outside this range of aluminum content.

### Conclusions

The preceding experiments demonstrate that all sheets of low carbon, aluminum-killed steel composition did not react uniformly to the conditions imposed. However, certain conditions were more conducive to the elongated grain shape than others. These were the conditions:

- 1—A residual aluminum content somewhat above 0.015 to about 0.066 pct.
- 2—Heating the hot-rolled strip to above the coarsening temperature and cooling relatively fast.
- 3—Coiling the hot-rolled strip near the lower critical temperature.
- 4—Cold reducing the hot-rolled strip without preliminary reheating.
- 5—Cold reducing the hot-rolled strip more than 30 pct.

6—Annealing after cold reduction using: a—A relatively slow heating rate, or b—A heat treatment at 700° to 1100°F preliminary to the final anneal.

This behavior can be explained by the following hypothesis: A supersaturated solid solution of aluminum nitride in steel is created by heating the material above the coarsening temperature and rapidly cooling to room temperature. This supersaturated solid is cold reduced. During the heating portion of the conventional annealing cycle, precipitation of aluminum nitride occurs to a major extent before the recrystallization temperature is reached. The development of more equiaxed grain structures by fast heating indicates that in this case recrystallization and grain growth takes place before precipitation.

This precipitation during slow heating takes place principally at preferred locations such as boundaries of grains elongated by cold reduction. The pre-

cipitate forms a mechanical obstruction to normal recrystallization and results in an elongated grain shape retaining part of the elongation imposed by cold reduction. When the supersaturated solid solution is heated before cold reduction, the nitride is believed to precipitate in a manner which does not influence the final grain shape. After such heating the precipitate resides in the hot-rolled strip grain boundaries and remains out of solution during cold reduction and annealing. After such material has been cold reduced, recrystallization during annealing results in an equiaxed grain structure.

The effectiveness of the compound in controlling grain shape is most pronounced in the same limited range of residual aluminum content most favorable for promoting fine grained behavior of the austenite. When heated, a re-solution of the compound takes place only at or above the austenite grain coarsening temperature. It appears that aluminum nitride

Table VIII. Residual Aluminum, Nitrogen Content as Aluminum Nitride, and Grain Shape of Samples Containing Variations in Residual Aluminum Content

| Heat, Sample | Residual Aluminum, Pct | Nitrogen Content as Aluminum Nitride, Pct |                              |                              | Grain Shape As Cold-Reduced and Annealed* |
|--------------|------------------------|-------------------------------------------|------------------------------|------------------------------|-------------------------------------------|
|              |                        | As Hot-Rolled                             | As Cold-Reduced and Annealed | As Cold-Reduced and Annealed |                                           |
| 1A           | 0.015                  | 0.0002                                    | 0.0044                       |                              | X                                         |
| B            | 0.043                  | 0.0008                                    | 0.0046                       |                              | E                                         |
| C            | 0.108                  | 0.0044                                    | 0.0047                       |                              | R                                         |
| D            | 0.146                  | 0.0044                                    | 0.0049                       |                              | R                                         |
| E            | 0.197                  | 0.0045                                    | 0.0053                       |                              | R                                         |
| 2A           | 0.034                  | 0.0001                                    | 0.0027                       |                              | E                                         |
| B            | 0.058                  | 0.0002                                    | 0.0027                       |                              | E                                         |
| C            | 0.066                  | 0.0003                                    | 0.0034                       |                              | E                                         |
| D            | 0.094                  | 0.0006                                    | 0.0029                       |                              | X                                         |
| E            | 0.142                  | 0.0008                                    | 0.0029                       |                              | R                                         |

\* E = elongated; X = intermediate; R = round or equiaxed.

not only inhibits development of equiaxed grain structure of cold-reduced ferrite, but is also largely responsible for the fine grained behavior of aluminum-killed steel in the austenite range; in the former case when the steel is supersaturated with respect to aluminum nitride prior to cold reduction and heated slowly for annealing, and in the latter case when the aluminum nitride is precipitated during heating to the austenitizing temperature.

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Table VII. Correlation of Nitrogen Content as Aluminum Nitride with Grain Size after Heating to Temperatures of 1700° to 2100°F

| Sample | Nitrogen Content as Aluminum Nitride, Pct |          |          |          |          |
|--------|-------------------------------------------|----------|----------|----------|----------|
|        | 1700°F                                    | 1800°F   | 1900°F   | 2000°F   | 2100°F   |
| 1      | 0.0032 F*                                 | 0.0032 F | 0.0024 F | 0.0006 C | 0.0002 C |
| 2      | 0.0048 F                                  | 0.0047 F | 0.0043 F | 0.0027 M | 0.0006 C |
| 3      | 0.0040 F                                  | 0.0041 F | 0.0043 F | 0.0023 M | 0.0007 C |
| 4      | 0.0039 F                                  | 0.0038 F | 0.0041 F | 0.0018 C | 0.0003 C |
| 5      | 0.0046 F                                  | 0.0038 F | 0.0041 F | 0.0012 M | 0.0002 C |

\* F = fine grain; M = mixed grain; C = coarse grain.



# Isothermal Formation of Martensite at Subzero Temperatures in a High Chromium Steel

by S. C. Das Gupta and B. S. Lement

Isothermal formation of martensite occurs in the range of  $-65^{\circ}$  to  $-197^{\circ}\text{C}$  and is always preceded by some athermal transformation. By rapid cooling the isothermal, but not the athermal, component of transformation can be suppressed. Stabilization against isothermal transformation can be induced by cycling from below  $M_s$  to room temperature.

**A**LTHOUGH the transformation of austenite to martensite is generally believed to occur only on cooling, recent evidence indicates that this reaction can also occur at constant temperature. Isothermal formation of martensite was observed in tool steel by Fletcher, Averbach, and Cohen.<sup>1,2</sup> They found that the hardening reaction that occurs during the quenching of a plain carbon or low carbon alloy tool steel does not stop immediately when room temperature is reached; instead austenite continues

to transform at room temperature although at a decreasing rate. Since only a small amount of austenite transforms in this fashion, isothermal formation of martensite was considered to be merely a "tailing off" effect of the main hardening reaction.

Another point of view was advanced by Kurdjumov and Maksimova<sup>3,4</sup> who reported that the austenite-martensite reaction could be suppressed by rapid cooling of a 6 pct Mn-0.6 pct C steel in liquid nitrogen and that as much as 25 pct martensite could be formed by reheating to and holding at subzero temperatures above that of liquid nitrogen. These investigators came to the conclusion that martensite is thermally nucleated at certain special regions in the austenite and subsequently grows to observable dimensions.

Isothermal transformation of austenite to martensite was cited by Fisher, Hollomon, and Turnbull<sup>5</sup> as evidence supporting another nucleation and growth theory of martensite formation. According

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This paper represents part of a thesis by S. C. Das Gupta submitted in partial fulfillment of requirements for the degree of Doctor of Philosophy in Metallurgy to the University of Notre Dame.

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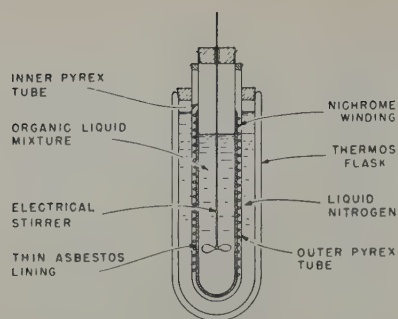


Fig. 1—Subzero furnace.

to this theory, at certain subzero temperatures the rate of growth of athermally formed martensite nuclei becomes slow enough so that isothermal transformation is measurable. This point of view was disputed by Kulin and Cohen<sup>6</sup> who showed that transformation of austenite to martensite is possible at a temperature as low as  $-266^{\circ}\text{C}$ , where a negligible rate of growth is predicted by the nucleation and growth theory.<sup>5</sup>

A new mechanism involving nucleation of strain embryos has been advanced by Cohen, Machlin, and Paranjpe<sup>7</sup> to explain the austenite-martensite transformation. According to these investigators isothermal transformation is due to temperature fluctuations which supply sufficient energy to complete the "shearing over" to martensite of strain embryos initially below a critical "shear" angle.

The present investigation was carried out to obtain additional information with respect to isothermal transformation at subzero temperatures. In order to check whether the phenomena reported by Kurdjumov and Maksimova<sup>8</sup> are of general occurrence, a high chromium steel having essentially the same transformation range as reported for their manganese steel was selected for this investigation.

### Experimental Details

**Chemical Composition:** The chemical composition of the steel investigated is as follows: C, 0.73; Mn, 0.28; Si, 0.20; S, 0.02; P, 0.02; and Cr, 14.84. This steel is from the identical heat used in the investigation of Klier and Troiano<sup>9</sup> to determine the effect of chromium and carbon contents on the  $M_s$  temperature.

**Austenitizing Treatment:** Specimens approximately  $1/16 \times 1/8 \times 1/4$  in. were sealed in an evacuated quartz tube and then austenitized for 2 hr at  $1275^{\circ}\text{C} \pm 5^{\circ}\text{C}$  in a platinum-rhodium wound tube furnace. This treatment which resulted in a grain size of A.S.T.M. No. 1-2 was selected on the basis of obtaining complete carbide solution.

Table I. Time Required to Reach Temperature

| Operation    | Initial Temperature, $^{\circ}\text{C}$ | Final Temperature, $^{\circ}\text{C}$ | Medium at Final Temperature | Time Required, Sec |
|--------------|-----------------------------------------|---------------------------------------|-----------------------------|--------------------|
| Subcooling   | 5                                       | -60 - -150                            | Organic liquid              | 18 $\pm$ 3         |
| Subcooling   | 5                                       | -197                                  | Liquid nitrogen             | 10 $\pm$ 3         |
| Up-quenching | -197                                    | -150 - -40                            | Organic liquid              | 15 $\pm$ 3         |
| Up-quenching | -197                                    | 20                                    | Water                       | less than 3        |

**Quenching Procedure:** Quenching was carried out in a 10 pct brine solution maintained at a temperature of  $5^{\circ}\text{C}$ . The quartz tube containing about five specimens was quickly transferred from the austenitizing furnace to the brine quench, and the tube was broken immediately. The breaking into a vacuum resulted in an efficient quenching action since 100 pct austenite was retained at  $5^{\circ}\text{C}$ .

**Subzero Cooling:** After quenching the specimens were placed in a subzero furnace maintained within  $\pm 1^{\circ}\text{C}$  of a selected temperature in the range of  $-60^{\circ}$  to  $-150^{\circ}\text{C}$ . The details of the subzero furnace are shown in Fig. 1. This furnace operates on the same principle as an ordinary resistance wound furnace; however, instead of room temperature at the outside of the furnace, liquid nitrogen in a thermos flask is used to provide an outside temperature of  $-197^{\circ}\text{C}$ . The inner pyrex tube contains an organic liquid mixture consisting of 75 pct petroleum ether and 25 pct methylcyclohexane, which has a freezing point of just under  $-150^{\circ}\text{C}$ . Temperature uniformity as well as a rapid rate of either subcooling or up-quenching is brought about by means of a stirrer. The times required for the centers of  $1/16 \times 1/8 \times 1/4$  in. specimens to reach within  $1^{\circ}\text{C}$  of selected temperatures using the subzero furnace were found to be as given in Table I. According to these results, subcooling in liquid nitrogen at  $-197^{\circ}\text{C}$  is more rapid than in the organic liquid maintained as low as  $-150^{\circ}\text{C}$ ; and up-quenching in water at  $20^{\circ}\text{C}$  is more rapid than in the organic liquid maintained as high as  $-40^{\circ}\text{C}$ .

**Metallographic Analysis:** Quantitative determination of the extent of transformation to martensite was carried out by the method of lineal analysis developed by Howard and Cohen.<sup>8</sup> The precision of measurement is estimated to be  $\pm 1$  pct martensite for the amounts of this constituent encountered in the present investigation. After a subzero treatment, specimens were mounted in bakelite, metallographically polished, and etched with a modified Vilella's reagent. Although the martensite plates are not darkened by this procedure, the boundaries become sufficiently sharp so that no difficulty is experienced in distinguishing between the two constituents.

It was found that the amount of martensite increases with distance below the surface of transformed specimens and reaches an approximately constant value at a depth of about 0.010 in. It is believed that this effect is due to residual stress set up on quenching from  $1275^{\circ}$  to  $5^{\circ}\text{C}$ . Since no transformation occurs during such quenching, it would be expected that due to differences in cooling rate compressive stresses are set up at the surface and tensional stresses at the interior. On subsequent cooling to subzero temperatures, the transformation is apparently hindered by the presence of compressive stresses at the surface. The amounts of martensite reported in this investigation were measured at a depth of 0.020 in. and are representative of the interiors of the specimens where tensional stresses apparently do not cause any appreciable variation.

### Results

**Martensite Formed on Cooling:** The amount of martensite formed on cooling is shown in Fig. 2. In this experiment a specimen was kept in the subzero furnace just long enough to reach the temperature of the organic liquid bath and then up-quenched



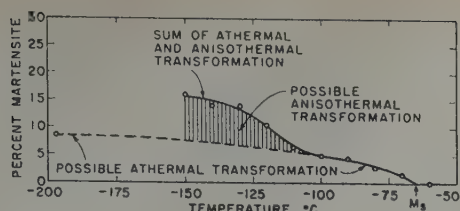


Fig. 2—Amount of martensite formed as a function of temperature in a 15 pct Cr-0.7 pct C steel austenitized 2 hr at 1275°C.

immediately to 20°C in water. The  $M_s$  temperature was found to be  $-65^\circ\text{C} \pm 5^\circ\text{C}$ . This is in agreement with the results of Klier and Troiano<sup>8</sup> who found a  $M_s$  temperature of between  $-38^\circ$  and  $-77^\circ\text{C}$  for  $\frac{1}{4} \times \frac{1}{4} \times \frac{1}{4}$  in. specimens heat treated in a similar fashion. However, although these investigators report that holding 1 hr at room temperature prior to subcooling lowers  $M_s$  to below  $-77^\circ\text{C}$ , this was not confirmed. In fact, reheating as-quenched specimens to a series of temperatures as high as 500°C for 1 hr prior to subzero cooling likewise was not found to have any appreciable effect on the  $M_s$  temperature.

On cooling below the  $M_s$  temperature the amount of martensite increases progressively and apparently reaches a maximum at about  $-150^\circ\text{C}$ , which is the lowest temperature that can be obtained with the organic liquid used. However, specimens cooled to the temperature of liquid nitrogen ( $-197^\circ\text{C}$ ) were found to contain about 7 pct less martensite than specimens cooled to  $-150^\circ\text{C}$ . This anomaly indicates that the austenite-martensite reaction in this steel can be partially suppressed by rapid cooling in liquid nitrogen. There appears to be a limit to the extent of this suppression since decreasing the specimen thickness from 0.070 to 0.020 in., which should effectively increase the cooling rate, does not change the amount of martensite formed on subcooling in liquid nitrogen to  $-197^\circ\text{C}$ . In fact, a thickness of 0.010 in., which is commensurate with the austenite grain size, actually results in a small increase in the amount of martensite at  $-197^\circ\text{C}$ . Possibly, this increase is due to the greater freedom from constraints to local change of shape associated with transformation in a single crystal of austenite as compared to polycrystalline austenite.

On the basis of these experiments it appears that subcooling in the organic liquid to temperatures above  $-150^\circ\text{C}$  does not result in purely athermal\* martensite but rather a combination of athermal and anisothermal\*\* martensite. The possible extent of anisothermal transformation is indicated by the extrapolation from  $-100^\circ$  to  $-197^\circ\text{C}$  in Fig. 2. By rapid subcooling it appears possible to suppress the anisothermal transformation but not the athermal transformation. Since the transformation occurs anisothermally, which means that it is time-dependent as

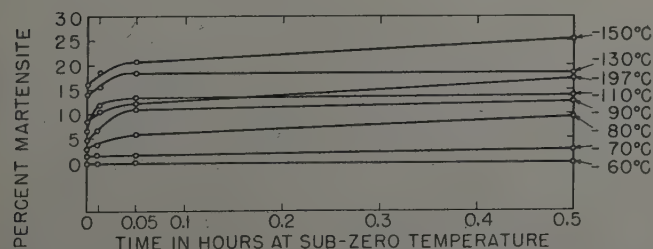


Fig. 3—Isothermal formation of martensite at various subzero temperatures in a 15 pct Cr-0.7 pct C steel austenitized 2 hr at 1275°C.

well as temperature-dependent, isothermal† transformation would also be expected to occur.

**Isothermal Martensite Formation:** The amount of martensite formed as a function of time at a series of constant subzero temperatures is shown in Fig. 3. Isothermal transformation of austenite to martensite was found to occur at temperatures ranging from  $-70^\circ$  to  $-197^\circ\text{C}$ . The rate of isothermal transformation decreases with time and becomes very slow after about 0.05 hr at all temperatures. The observable initial rate of isothermal transformation increases with decreasing temperature, reaches a maximum at about  $-110^\circ\text{C}$ , and progressively decreases below this temperature. If the amount of martensite is plotted against log time as in Fig. 4, the course of the reaction can apparently be represented by a straight line plot after about 0.01 hr.

Isothermal formation of martensite was found to occur as low as  $-197^\circ\text{C}$  and as much as 14 pct martensite forms after 24 hr at this temperature. This is shown by a series of micrographs in Fig. 5. It was observed that isothermal transformation occurs

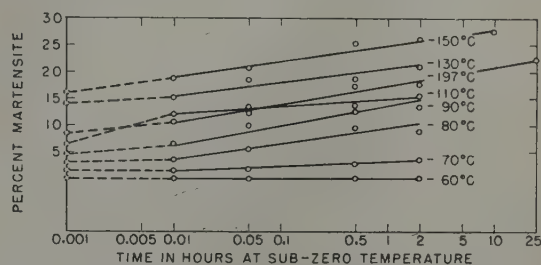


Fig. 4—Semi-log plot showing isothermal formation at various subzero temperatures in a 15 pct Cr-0.7 pct C steel austenitized 2 hr at 1275°C.

mainly by the formation of new martensite plates rather than thickening of existing plates. Except for a larger number of smaller size plates due to the partitioning effect of increased transformation, the appearance of martensite formed isothermally was found to be the same as that formed athermally.

Holding as-quenched specimens for 1 hr at  $20^\circ\text{C}$  prior to cooling to subzero temperatures was not found to have any appreciable effect on isothermal transformation. Here again evidence of appreciable stabilization above the  $M_s$  temperature prior to cooling below the  $M_s$  temperature is lacking.

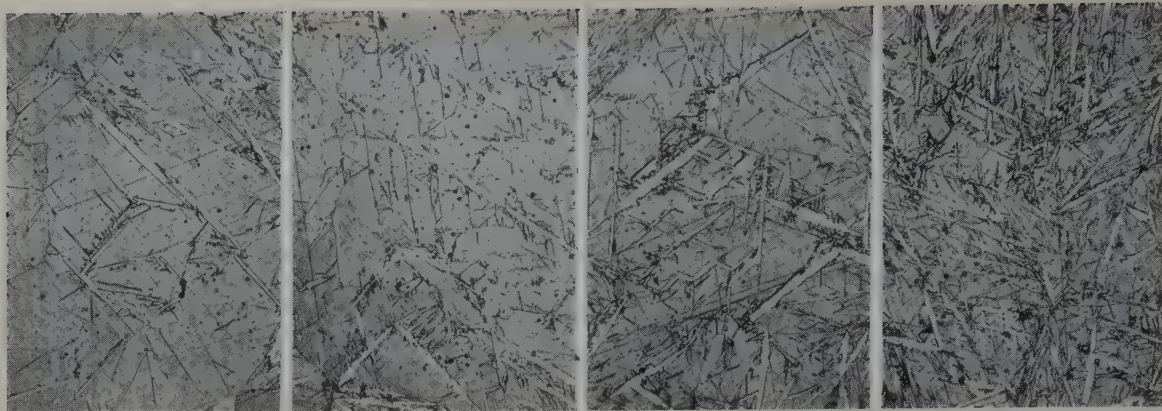
**Effect of Cycling on Isothermal Transformation:** The effects of cycling between  $20^\circ$  and  $-95^\circ\text{C}$  and between  $20^\circ$  and  $-150^\circ\text{C}$  on isothermal transformation were studied. The treatments used are illustrated in Fig. 6 and the results are given in Table II.

In treatments A, B, and C the total time at the subzero temperature is 30 min. Up-quenching to  $20^\circ\text{C}$  immediately after reaching the subzero temperature (treatment A) or after holding 3 min at the subzero temperature (treatment B) results in less martensite formation than does an uninterrupted hold at the subzero temperature (treatment C). In treatments A and B virtually complete stabilization results from up-quenching to  $20^\circ\text{C}$  and therefore the subsequent hold at the subzero temperature is ineffective in producing additional transformation. Since in both these cases some martensite is present before up-quenching to  $20^\circ\text{C}$ , these results indicate that partial transformation may be required before stabilization can occur in this steel. This suggests

\* Athermal — dependent on temperature.

\*\* Anisothermal — dependent on cooling rate.

† Isothermal — dependent on time (for a given temperature).



Zero time at  $-197^{\circ}\text{C}$ .

3 min at  $-197^{\circ}\text{C}$ .

2 hr at  $-197^{\circ}\text{C}$ .

24 hr at  $-197^{\circ}\text{C}$ .

Fig. 5—Micrographs showing isothermal transformation at  $-197^{\circ}\text{C}$  in a 15 pct Cr-0.7 pct C steel. X150.

that partial transformation stimulates subsequent isothermal transformation and that heating to  $20^{\circ}\text{C}$  wipes out the stimulating effect.

**Isothermal Transformation after Up-quenching from  $-197^{\circ}\text{C}$ :** The effect of cooling to  $-197^{\circ}\text{C}$  followed by up-quenching to and holding at various subzero temperatures is shown in Fig. 7. These experiments were carried out in order to study the effect of a constant initial amount of martensite on subsequent isothermal transformation at various temperatures. Series A specimens were held 3 min at  $-197^{\circ}\text{C}$ , which resulted in the formation of about 11 pct martensite prior to up-quenching. Series B specimens were held 2 hr at  $-197^{\circ}\text{C}$ , which resulted in the formation of about 17 pct martensite prior to up-quenching. In both series up-quenching to temperatures as high as  $-40^{\circ}\text{C}$  results in additional transformation prior to isothermal holding. The increases amount to about 6 pct martensite for series A and about 4 pct martensite for series B. The constancy of these amounts for a given series suggests that the additional transformation occurred during the short period of time the temperature passed through the range of  $-197^{\circ}\text{C}$  to about  $-150^{\circ}\text{C}$ .

At all temperatures below  $-70^{\circ}\text{C}$ , series A specimens show a higher initial rate of isothermal transformation than do series B specimens. This indicates that an increase in the initial amount of mar-

tensite from 17 to 21 pct results in a decrease in the rate of isothermal transformation at a given temperature. Since a larger initial amount of martensite would be expected to exert a greater stimulating effect on isothermal transformation, the observed decrease may be due to the greater influence of partitioning. Because of this effect, the larger the amount of initial transformation, the smaller the volume generated by nucleation of each martensite plate. Partitioning also may slow down transformation by increasing constraints to the local change of shape required by the formation of each new plate.

For both series the observable initial rate of isothermal transformation is apparently higher at  $-150^{\circ}\text{C}$  than at  $-197^{\circ}\text{C}$  and very low or zero just below the  $M_s$  temperature. For series A a maximum initial rate occurs at a temperature judged to be about  $-140^{\circ}\text{C}$ . Since these experiments were carried out keeping the initial amount of martensite constant, the observed temperature dependence of initial rate of transformation should be a direct consequence of the temperature dependence of rate of nucleation of martensite plates. This assumes that the generation of such plates, once nucleated, is practically instantaneous.

### Discussion of Results

The 15 pct Cr-0.7 pct C steel investigated was found to have a fairly definite  $M_s$  temperature of  $-65^{\circ}\text{C} \pm 5^{\circ}\text{C}$  corresponding to the particular austenitizing treatment of 2 hr at  $1275^{\circ}\text{C}$  employed. Isothermal formation of martensite was found to occur below this  $M_s$  temperature and is apparently always preceded by some athermal formation of martensite. Since it was not found possible to differentiate between athermal and isothermal martensite by metallographic examination, it appears that the mechanism of formation is essentially the same whether martensite forms on cooling or at constant tempera-

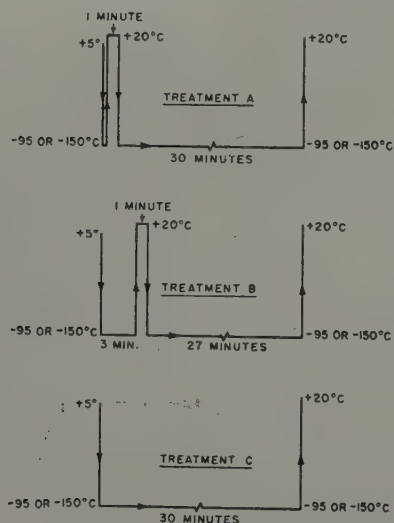


Fig. 6—Schematic representation of cyclic treatments used in investigation of stabilization effect.

Table II. Effect of Cycling on Isothermal Transformation

| Temperature of Subzero Isothermal Run, $^{\circ}\text{C}$ | Percent Martensite |              |              |
|-----------------------------------------------------------|--------------------|--------------|--------------|
|                                                           | Treatment A*       | Treatment B* | Treatment C* |
| -95                                                       | 4.0                | 8.8          | 10.3         |
| -150                                                      | 18.3               | 19.6         | 23.8         |

\* See Fig. 6.



ture. The rate of the reaction seems to be governed by the rate of nucleation of martensite plates rather than their rate of "growth" which appears practically instantaneous at all temperatures studied.

The isothermal behavior of the chromium steel was found to be similar to that of the manganese steel investigated by Kurdjumov and Maksimova.<sup>3</sup> The following points of similarity were observed. Isothermal transformation of austenite to martensite was found to occur at subzero temperatures below  $-65^{\circ}\text{C}$ . Such transformation occurs either after cooling directly to a subzero temperature below  $-65^{\circ}\text{C}$ , or after first subcooling to the temperature of liquid nitrogen ( $-197^{\circ}\text{C}$ ) and then up-quenching to the selected subzero temperature. The observable initial rate of isothermal transformation goes through a maximum with decrease in temperature below  $-65^{\circ}\text{C}$ .

It was not found possible to suppress completely the austenite-martensite reaction in the chromium steel by cooling to the temperature of liquid nitrogen ( $-197^{\circ}\text{C}$ ) as claimed by Kurdjumov and Maksimova<sup>3</sup> for their manganese steel. Confirmation of the results of Kurdjumov and Maksimova by other investigators is necessary in order to establish whether complete suppression can actually be attained. Thus far, attempts to accomplish this have proved unsuccessful<sup>6</sup> and it is probable that the reported chemical composition of the manganese steel<sup>3</sup> is erroneous.

The phenomenon of stabilization which plays an important role in isothermal transformation was not investigated by Kurdjumov and Maksimova.<sup>3</sup> This phenomenon apparently is a result of removing the stimulating effect of partial transformation by thermal means. Stabilization is nicely explained by the strain embryo theory<sup>7</sup> according to which transformation to martensite generates strain embryos that can be relaxed by stress relief even at relatively low temperatures. That partial transformation is necessary before austenite can be stabilized against further transformation on cooling was pointed out by Harris and Cohen.<sup>10</sup> The occurrence of extremely rapid stabilization resulting from interrupting the quench at room temperature prior to cooling below  $M_s$  as claimed by Klier and Troiano<sup>8</sup> was not investigated in the present work. The possible relationship of such a phenomenon to isothermal transformation merits further study.

As indicated by the results of this investigation, isothermal transformation of martensite is influenced by the temperature dependence of rate of nucleation of martensite plates, the stimulating effect of partial transformation, the geometrical effect of partitioning, and the previous history with respect to stabilization. A more detailed knowledge of these factors is required in order to judge the validity of the current theories of the mechanism of the austenite-martensite transformation.

### Summary

The following characteristics of the austenite-martensite transformation have been observed in a 15 pct Cr-0.7 pct C steel:

- 1—Partial but not complete suppression of martensite is attainable by quenching to  $-197^{\circ}$  in liquid nitrogen. The part of the transformation that is suppressible probably corresponds to the isothermal rather than the athermal component of the transformation.

- 2—Isothermal transformation occurs at subzero temperatures below  $-65^{\circ}\text{C}$  which is the  $M_s$  point

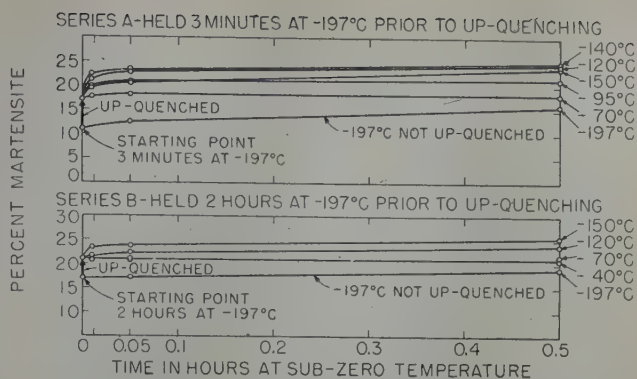


Fig. 7—Isothermal formation of martensite following up-quenching a 15 pct Cr-0.7 pct C steel from  $-197^{\circ}\text{C}$  and holding at various subzero temperatures. Austenitizing treatment consisted of 2 hr at  $1275^{\circ}\text{C}$ .

corresponding to an austenitizing treatment of 2 hr at  $1275^{\circ}\text{C}$  followed by water quenching to  $5^{\circ}\text{C}$  and then subcooling in an organic liquid.

- 3—Isothermal transformation is always preceded by some athermal transformation and occurs mainly by the formation of new plates rather than the growth of existing plates.

- 4—The observable initial rate of isothermal transformation goes through a maximum with decrease in temperature below the  $M_s$  point.

- 5—Stabilization against isothermal transformation at a given subzero temperature results from cycling between that temperature and room temperature.

### Acknowledgments

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# Desulphurization of Pig Iron with Pulverized Lime

by Bo Kalling, C. Danielsson, and Ottar Dragge

THE desulphurizing of pig iron has been accomplished with a number of different additions. The oldest and still most commonly used agent is soda, the extensive use of which commenced about 1925, when it was used principally for cupola furnace iron. More recent experience<sup>1</sup> seems to show that better results can be obtained with sodium hydroxide. The well-known desulphurizing properties of lime have also been exploited in different technical processes. Another material with even more powerful effect is calcium carbide.<sup>2</sup> The desulphurizing ability of manganese, when added to the ladle in sufficient quantity, should also be mentioned in this connection. During recent years increasing attention has been paid to the desulphurizing properties of metallic magnesium.<sup>3</sup> An addition of a suitable alloy of magnesium is now in use purely for the purpose of sulphur elimination.

Of the desulphurizing agents mentioned, lime is by far the cheapest, provided that the reaction can be brought about rapidly and completely. Therefore, a method that makes full use of the desulphurizing ability of lime may be able to compete with other processes. A method developed at the Domnarfvet Iron and Steel Works (Sweden) will be described, which enables pig iron to be rapidly desulphurized to very low sulphur contents by using a burnt lime powder as the desulphurizing agent.

## Lime in Older Processes

In cases where lime has been used for the desulphurization of pig iron, it has generally not been used alone, but mixed with other substances such as fluorspar, to obtain the formation of a molten slag during the process. This method has been tried by Tigerschiöld,<sup>4</sup> who treated the iron with a lime-fluorspar mixture, the stirring of the iron being brought about inductively with low frequency alternating current. Very good results were obtained. A process of this type has also been suggested by R. P. Heuer, U. S. A. The principles of this method, which has been tested in Great Britain by Newell, Langner, and Parsons,<sup>5</sup> are that a mixture of lime and fluorspar is added to the hot metal in the ladle, while a powerful stream of nitrogen gas is blown into the bath to produce the required intermixing. The results of the tests were unsatisfactory, however. A similar process has been developed at The Steel Co. of Canada, according to a statement by H. M. Griffith.<sup>6</sup> Here the tests were carried out in a carbon-lined ladle provided with carbon tuyeres in the side wall for blowing nitrogen into the bath. The addition consisted of about 20 lb of a mixture of burnt lime and fluorspar per ton of pig iron. Good results appear to have been achieved. The sulphur content of the pig iron is stated to have been reduced from 0.025 to 0.050 pct down to 0.006 pct.

Various methods of desulphurizing pig iron have

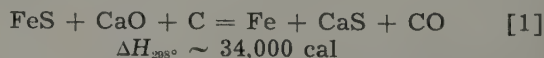
been tried using lime powder without fluxing material for fusing. Eichholz and Behrendt<sup>7</sup> have experimented with blowing a powdered lime-coke mixture with air into the ladle. Their results were, however, not conclusive and the experiments do not appear to have been continued. Similar experiments have been carried out at Domnarfvet, using nitrogen instead of air in order to avoid oxidation. But these attempts were not particularly successful. It appears to be difficult to achieve the required agitation by this means. The strong cooling effect of the gas on the iron is also a serious drawback.

A method in many respects similar to that tried at Domnarfvet was tried by Eulenberg and Krus at the end of the 1930's. Here again desulphurization was carried out with lime alone, brought into contact with the molten iron in a rotary furnace. The temperature was kept at the required level, 1400° to 1500°C, by the introduction of a pulverized coal burner in one end of the furnace. The speed of rotating was not given. A paper by Bading and Krus<sup>8</sup> states that, in one of the first experiments, the sulphur content in 56 tons of pig iron was brought down from 0.186 to 0.035 pct in 117 min, but that a considerable shortening of the time would be possible. According to later reports by Eichholz and Behrendt,<sup>7</sup> it should be possible by this process to achieve a desulphurization speed of 0.35 pct S per hr for a consumption of 6 to 10 pct limestone and 2 to 3 pct coke, as fuel exclusively. The final sulphur content is, however, not stated.

## Domnarfvet Method

After a number of different procedures had been investigated, the tests at Domnarfvet were directed to desulphurization with lime in a rotary furnace. Before going into the practical details of the method, the theoretical aspects will be discussed briefly.

If the pig iron does not contain alloying elements other than carbon, the reaction can be expressed most simply by the usual equation:



That this reaction can be carried through to a very complete desulphurization of pig iron has been shown by Oelsen<sup>9</sup> in a discussion in connection with the Eulenberg and Krus' method. He mentions two laboratory tests, in one of which the sulphur content in the pig iron at 1400°C was reduced from 0.540 to 0.006 pct after treating with 3.35 pct lime. The pig iron had a low manganese content, but other analysis is not given.

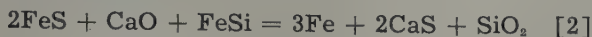
Mention also should be made of the recently published investigations by Fischer and Cohnen<sup>10</sup> dealing with the influence of the carbon content of the iron on desulphurization with lime, although in this case fluorspar was added also. The tests show that efficient desulphurization is possible with lime in the steel bath, provided that the carbon content is sufficiently high. The temperature employed in these tests was considerably higher (1620°) than that normal for treatment of pig iron. The author concludes that the product  $\text{S}\% \times \text{C}\% = 0.011$  at the temperature in question.

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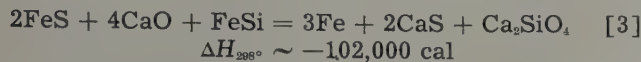
Discussion on this paper, TP 3109C, may be sent, 2 copies, to AIME by Oct. 1, 1951. Manuscript, Feb. 27, 1951. St. Louis Meeting, February 1951.



In practice the conditions are complicated by the fact that the pig iron to be desulphurized is very seldom free of silicon. In a pig iron containing silicon above a certain level, the carbon is replaced by silicon as a reducing agent, and the reaction equation may be written:



The silica reacts with the lime present to form a silicate, presumably  $\text{Ca}_2\text{SiO}_4$ , in the main, when there is an excess of lime. The reaction equation will then be:



The formation of silicate here implies that a large part of the lime is bound to the silica, so that the consumption of lime may be much higher in this case than that with silicon-free iron.

How far reaction 3 can be carried, when desulphurizing to a certain sulphur content in the pig iron, is difficult to estimate reliably. A knowledge is required, for instance, of the intersolubility of

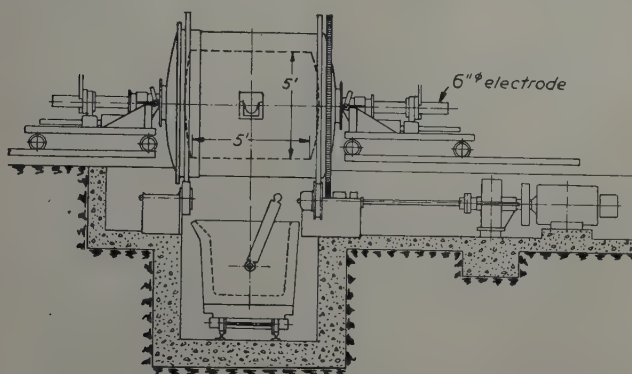


Fig. 1—Diagram of furnace showing layout and dimensions.

the different components. Their solubility is probably very limited, so the reaction should be nearly complete even in desulphurizing to a low sulphur content in the pig iron. On the assumption that transformation takes place completely according to eq 3 and that 0.1 pct S is eliminated, the following data are obtained, whatever the sulphur content in the pig iron during treatment: lime consumption, 0.35 pct of the weight of pig iron; oxidation of silicon, 0.05 pct; S and  $\text{SiO}_2$  content of lime product, 20 and 19 pct, respectively.

Some of the test results presented in the following indicate that while the theoretical consumption of lime is roughly that stated above, in practice certain cooperative factors make it necessary to calculate with a considerably higher consumption of lime.

It should be pointed out that reduction with carbon, as above, is endothermic, while silicon reduction is exothermic. The equilibrium of the carbon reaction should therefore be displaced towards lower sulphur contents at a higher temperature, while the opposite applies to reduction with silicon. But since equilibrium for an excess of lime corresponds in both cases to an extremely low sulphur content in the iron, the temperature has no great influence on the reaction. Nor does the temperature appear particularly to affect the rate of reaction within the normal temperature range applying here. The evolution of heat in the silicon reaction is valuable, as the temperature loss in the treatment of the hot metal is thus counteracted to a large extent.

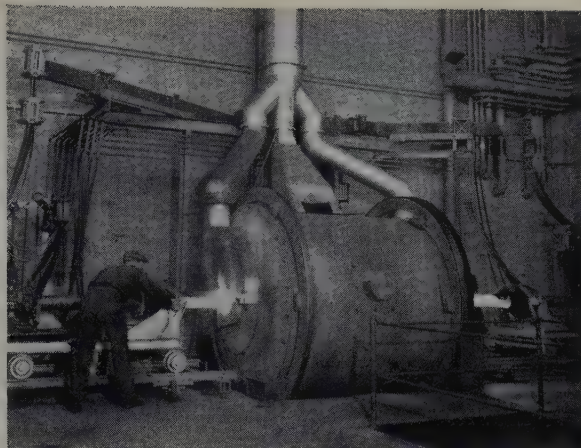


Fig. 2—Furnace as electrodes are being withdrawn.

The silicon content required within this temperature range for the reducing effect of the silicon to exceed that of the carbon, is certainly very low. Our experiments indicate that the reducing action of silicon is as great as that of saturated carbon at a silicon content of about 0.05 pct at  $1300^\circ\text{C}$ .

A matter of prime importance to the result of the process has proved to be that unnecessary oxidation of silicon should be avoided as far as possible. The silica formed opposes the reaction primarily by binding the lime as silicate, but also to a large extent by the silicate adhering to unused grains of lime and thus preventing the latter from intimate contact with the pig iron. The process should therefore take place under strongly reducing conditions. All oxidizing gases should be eliminated from the furnace during treatment. Therefore, the furnace should not be heated with combustion gases even if they are "reducing," i.e., contain unburnt carbon monoxide. As previously stated, even pure carbon monoxide has a strong oxidizing action on silicon in normal contents in the pig iron. The best result should be achieved then if the process is carried out in a closed furnace. Oxygen-free gases, hydrogen, and hydrocarbons, may nevertheless be supplied, which can be of advantage, as the presence of hydrogen should increase the reaction speed. But even when every possible step is taken to prevent external oxidizing gases from entering the furnace during the process, it is difficult to avoid some oxidation of silicon taking place apart from that occurring by the desulphurization reaction.

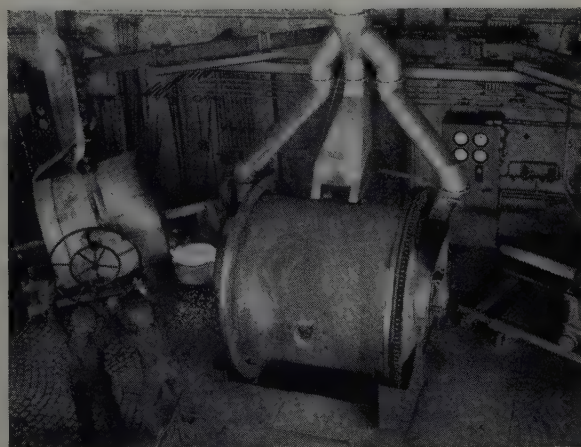


Fig. 3—Furnace during charging of pig iron.



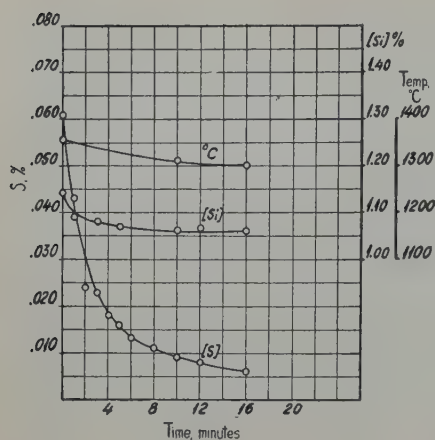
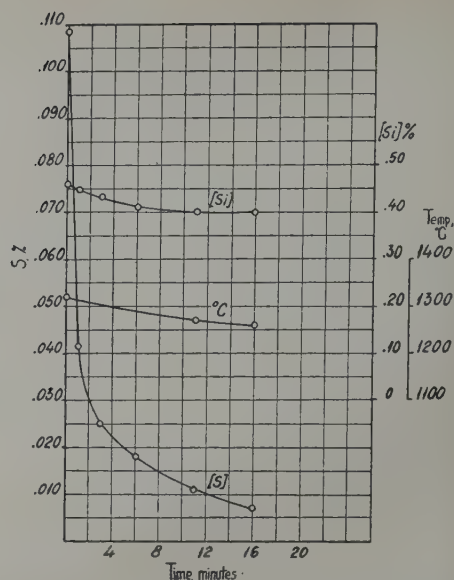


Fig. 4—(left) Heat KR8

Hot metal 2460 kg; C, 3.6 pct; 40 rpm. Lime powder, 39 kg; Mn, 1.1 pct. Coke powder, 10 kg; Si, 1.14 to 1.08 pct; P, 0.05 pct.

Fig. 5—(right) Heat A34

Hot metal, 2230 kg; C, 3.7 pct; 40 rpm. Lime powder, 45 kg; Mn, 0.5 pct. Coke powder, 45 kg; Si, 0.58 to 0.40 pct; P, 1.7 pct.



The lime must be in a very finely pulverized form if a sufficiently large contact surface is to be obtained with the hot metal. The tendency of fine grained lime to form balls must, however, be avoided. For this reason, the temperature of the hot metal must not be kept too high. A safety measure which is generally found desirable, but perhaps not always necessary, is to mix in a certain quantity of fine grained coke dust in the lime to counteract the tendency to stick.

If a rapid reaction is desired, an extremely intensive agitation of lime and hot metal is imperative. A short time of treatment is important not only for the saving in time, but also for the avoidance of an unnecessary temperature loss during the process, which, as stated above, should preferably be carried out without external heating. It has been found necessary to increase the speed of rotation of the furnace to a rate far above that employed with other rotary furnaces for metallurgical use. In this way the time of reaction can be lowered to only a few minutes.

### Results

The first tests with this method were started at Domnarfvet in 1947. They were made in a semiscale, cylindrical rotary furnace with a capacity of about 3 tons. Laboratory experiments were made later to study in greater detail the factors affecting the reactions and the states of equilibrium. This work has, however, not advanced so far that definitive results can be given. During the first half of 1950 operations were started in a plant for commercial use of the method at Surahammars Bruks AB, Surahammar, Sweden. The maximum capacity of the furnaces is about 18 tons. The results obtained from this plant are reported by S. Fornander.<sup>11</sup> The present paper will deal only with the results obtained from tests in the 3-ton furnace at Domnarfvet.

From Fig. 1, which shows the dimensions of the furnace, it can be seen that electrical heating was employed with graphite electrodes introduced through central openings in the two ends. Fig. 2 shows the furnace at a moment when the electrodes

are just being withdrawn, and Fig. 3, during the charging of the pig iron. The tapping of the hot metal and lime charge was made through the visible tap hole in the center of the furnace mantle.

In all experiments the furnace was lined with ordinary fire clay. Desulphurization can be carried through without any formation of balls or lime attack on the furnace lining, as long as the temperature of the pig iron does not exceed about 1350° to 1400°C. A more favorable result may be obtainable through the use of a basic furnace lining such as magnesite or tar-dolomite, or, perhaps even better, a carbon lining. Fire clay, however, has given such satisfactory results that there was no reason to

Table II. Chemical Analysis of the End Lime, in Percent

| Heat  | Fe*  | MnO  | CaO  | CaS  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | S    | C    | Na <sub>2</sub> O |
|-------|------|------|------|------|------------------|--------------------------------|------|------|-------------------|
| KR 16 | 5.0  | 0.23 | 69.0 | 8.8  | 7.6              | 1.7                            | 3.9  | 4.5  |                   |
| KR 18 | 3.4  | 0.34 | 67.8 | 10.6 | 10.8             | 2.3                            | 4.7  | 1.1  |                   |
| KR 22 | 10.1 | 0.39 | 36.8 | 27.0 | 7.3              | 1.6                            | 12.0 | 12.9 |                   |
| KR 25 | 2.1  | 0.34 | 62.2 | 13.1 | 15.3             | 2.6                            | 5.8  | 0.85 | 0.27†             |
| KR 34 | 9.5  | 0.35 | 51.6 | 14.6 | 17.4             | 2.2                            | 6.5  | 0.63 |                   |
| KR 36 | 12.1 | 1.03 | 49.6 | 18.2 | 14.6             | 2.7                            | 8.1  | 0.99 |                   |
| KR 40 | 9.8  | 1.07 | 55.1 | 11.0 | 8.0              | 3.2                            | 4.9  | 9.0  |                   |
| KR 41 | 4.4  | 1.59 | 28.4 | 35.1 | 17.1             | 2.4                            | 15.6 | 9.2  |                   |
| KR 42 | 8.4  | 0.23 | 45.0 | 18.2 | 10.8             | 3.1                            | 8.1  | 13.1 |                   |

\* The main part of the Fe content is probably in the metallic state.

† The Na<sub>2</sub>O content at the start of the heat corresponds to 4.4 pct Na<sub>2</sub>O at the end.

change to another material, and in any case it appears to be the most economical.

In most experiments the pig iron was first introduced into the furnace, after which a quantity of finely ground, burnt lime in suitable proportion to the pig iron was shovelled on to the surface of the bath, usually mixed with a varying quantity of coke powder. The screen analysis of the lime used is recorded in Table I. The lime charge contained a not inconsiderable amount of CO<sub>2</sub> and H<sub>2</sub>O, which caused a strong development of gas at the beginning of the treatment. After the gas evolution had ceased, the furnace was kept tightly shut. The rate of rotation was in most cases 40 rpm, which was the maximum for the furnace.

In Figs. 4 to 13 the course of desulphurization in a number of tests is shown, as is the change in the silicon content of the hot metal and the temperature loss during each treatment. The temperature of the

Table I. Grain Size of the Lime Powder Used

| Mesh    | A-heats, Pct | KR-heats, Pct |
|---------|--------------|---------------|
| >32     | 16.9         | 2.7           |
| 32-65   | 11.9         | 7.3           |
| 65-150  | 23.5         | 8.2           |
| 150-250 | 39.9         | 10.0          |
| <250    | 7.8          | 71.8          |
|         | 100.0        | 100.0         |



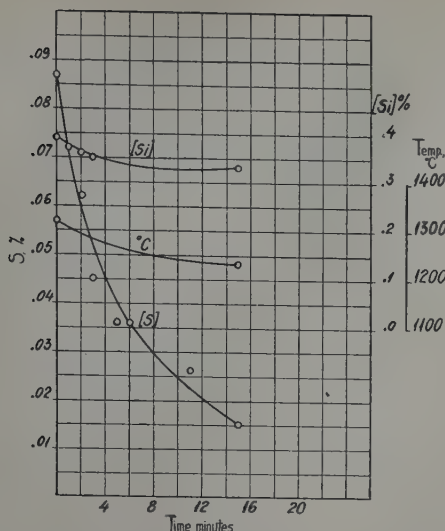
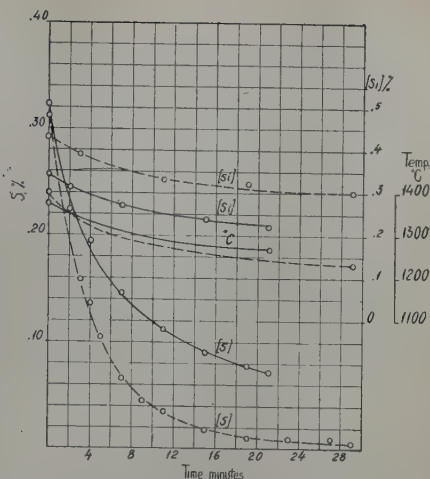


Fig. 6—(left) Heat KR36

Hot metal, 2690 kg; C, 3.0 pct; 40 rpm. Lime powder, 24 kg; Mn, 0.8 pct. Coke powder, 12 kg; Si, 0.39 to 0.53 pct; P, 1.8 pct.

Fig. 7—(right) KR41 and KR42

KR 41 (solid line) — Hot metal, 2880 kg; C, 3.6 pct; 40 rpm. Lime powder, 49 kg; Mn, 0.4 pct. Coke powder, 24 kg; Si, 0.34 to 0.22 pct; P, 2.1 pct.  
KR 42 (broken line) — Hot metal, 2640 kg; C, 3.7 pct; 40 rpm. Lime powder, 100 kg; Mn, 0.3 pct. Coke powder, 50 kg; Si, 0.43 to 0.30 pct; P, 2.2 pct.



furnace when the pig iron was introduced was normally about 1100°C.

Table II gives the analysis of the "end lime" obtained during treatment for the majority of heats. Prior to analysis, the major part of the metallic iron had been separated magnetically. The analysis applies to material having passed through a 65 mesh screen. Much of the product is admittedly coarser, but it was considered important to form a clear picture of how far the reaction could be taken with the finest material. The sulphur content has proved slightly higher in the analyses recorded than in an average sample of the end lime.

The silica content of the end lime does not originate only from the silicon oxidized in reaction 3. Some is obtained from silica in the lime and coke dust, and a varying quantity also from the lining. Generally a certain quantity of silica has been formed through the presence in the furnace of undesirable oxidizing substances, such as iron oxides and sulphates formed through oxidation of residues, in the furnace after tapping the previous charge, carbon dioxide and water vapor from the lime charge, etc. In Table III are recorded the proportions of the different sources of silica in the charges examined.

An attempt has been made to determine the "lime yield" in the different heats on the basis of the analyses, by which is meant the theoretical amount of lime required for the completion of reaction 3

Table III. Origin of the SiO<sub>2</sub> Found in the End Lime, in Percent

| Analysis on used materials:                 |          |          |          |          |                  |          |                                |          |          |  |
|---------------------------------------------|----------|----------|----------|----------|------------------|----------|--------------------------------|----------|----------|--|
|                                             | CaO      |          |          |          | SiO <sub>2</sub> |          | Al <sub>2</sub> O <sub>3</sub> |          |          |  |
| Lime                                        | 98.2     |          |          |          | 3.1              |          | 0.7                            |          |          |  |
| Coke                                        |          |          |          |          | 4.0              |          | 2.7                            |          |          |  |
| Lining                                      |          |          |          |          | 57.0             |          | 39.0                           |          |          |  |
| Heats                                       | KR<br>16 | KR<br>18 | KR<br>22 | KR<br>25 | KR<br>34         | KR<br>36 | KR<br>40                       | KR<br>41 | KR<br>42 |  |
| SiO <sub>2</sub> by reaction 3              | 43       | 37       | 0        | 32       | 35               | 50       | 8                              | 83       | 66       |  |
| SiO <sub>2</sub> from the coke ash          | 22       | 16       | 18       | 11       | 5                | 10       | 21                             | 7        | 12       |  |
| SiO <sub>2</sub> from charged lime          | 35       | 24       | 27       | 16       | 13               | 15       | 28                             | 11       | 19       |  |
| SiO <sub>2</sub> from the lining*           | †        | 8        | 16       | 10       | 9                | 13       | 29                             | 10       | 24       |  |
| SiO <sub>2</sub> through unwanted oxidation | †        | 15       | 39†      | 31       | 38               | 12       | 14†                            | -11§     | -21§     |  |

\* At continuous operation, the SiO<sub>2</sub> from the lining is expected to decrease to negligible values.

† The furnace is quite clean at the start of the heat.

‡ The main part of the unwanted SiO<sub>2</sub> content seems to originate from oxidation of products remaining in the furnace from the preceding heat.

§ Heats with both Si and C reduction during the desulphurization.

in proportion to the total quantity actually used. The somewhat doubtful assumption has thus been made that all silica is bound to lime in the form of Ca<sub>2</sub>SiO<sub>4</sub>, and that Al<sub>2</sub>O<sub>3</sub> and the insignificant MnO content need not be taken into consideration. The calculated lime yield therefore will probably be too high in some cases, which is partly shown by the fact that the free amount of CaO has been negative in one case (KR 41). Thus, all silica is not bound as Ca<sub>2</sub>SiO<sub>4</sub>, but is also in the form of other more acid silicates. The result of the calculations is given in Table IV.

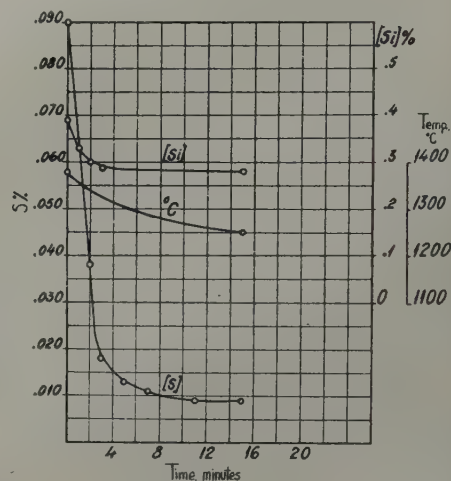
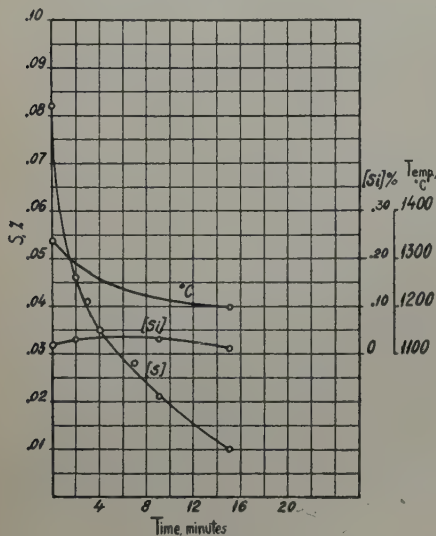
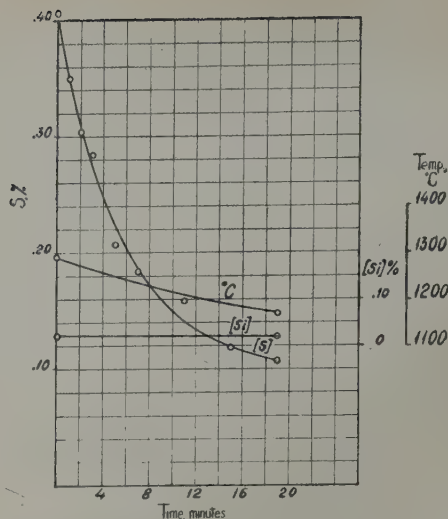
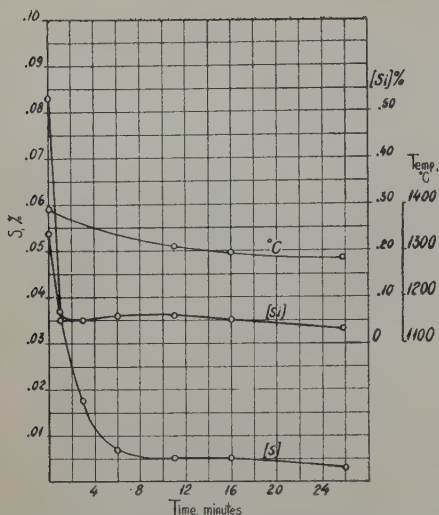
The coke added has, like the lime, been finely pulverized. The addition of coke generally has been about half that of lime. A large part of the coke, however, has been used up through dissolving of the carbon in the pig iron, which was not previously

Table IV. Calculated Partition of Original CaO in End Lime, Percent

| Heats                                         | KR 22 | KR 25 | KR 34 | KR 36 | KR 40 | KR 41 | KR 42 |
|-----------------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| CaO bound in Ca <sub>2</sub> SiO <sub>4</sub> | 24.1  | 39.5  | 51.7  | 42.8  | 23.5  | 57.4  | 34.2  |
| CaO transferred to CaS                        | 37.0  | 14.0  | 11.4  | 21.3  | 13.5  | 49.1  | 24.0  |
| Unused CaO                                    | 38.9  | 46.5  | 36.9  | 35.9  | 63.0  | -6.5  | 41.8  |
| Total                                         | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| "Yield" of CaO                                | 61.1  | 53.5  | 63.1  | 64.1  | 37.0  | 106.5 | 58.2  |

fully saturated with carbon. This is seen by the comparatively low carbon content in the end-lime analyses. In other cases, where the pig iron is high in silicon, there has been a considerable separation of graphite during the process, which means that a smaller amount of coke is required. How much coke is needed under different conditions has not been fully worked out, but that a certain, even if small, addition is desirable has been clearly shown from the experiments.

Figs. 4 to 6 show some normal heats. In the case of heat KR-8 a pig iron fairly high in silicon, but with low phosphorus content, has been treated, while the other two diagrams show the desulphurization of a basic bessemer pig iron of normal analysis. As will be seen, the desulphurization is very rapid if the amount of lime is sufficient, and about equally so whether the pig iron is high or low in silicon. The lesser amount of lime in experiment KR-36 (Fig. 6) caused a slower and less complete reaction. The experiment shows, however, that a considerable desulphurization can be obtained with the addition of only about 1 pct lime. The yield of lime, 58 pct according to Table IV, in this case is very satisfactory.



The silicon content in the pig iron sinks, in all cases, by about 0.05 pct, which shows that the losses through "foreign" oxidation have been negligible.

The temperature drop during the process is about 50°C (rather more in heat KR-36), which is satisfactory considering the small size of the furnace. It can be assumed that heating 1 pct dry carbon dioxide-free lime to the reaction temperature will cool the hot metal by about 15°. The corresponding figure for coke dust is about 25°. The heat of reaction in the presence of silicon, on the other hand, corresponds to an increase in the temperature of the hot metal by about 10° for oxidation of 0.05 pct Si. The resulting temperature drop in desulphurization of a pig iron containing about 0.1 pct S with 1.5 pct lime and 0.5 pct coke is calculated from these figures

to be about 25°. About 10° to 20° should always be added to cover radiation losses, etc.

Heats KR-41 and KR-42 in Fig. 7 are examples of how far desulphurization can be brought in one operation commencing with pig iron with a sulphur content of between 0.3 and 0.4 pct. In charge KR-42 the sulphur content has been brought down from 0.31 to under 0.003 pct when using 3.8 pct lime, i.e., an elimination of 99 pct. The lime yield is high notwithstanding, 58 pct according to the calculations. In heat KR-41, where the addition of lime was only half as great, 1.9 pct, the sulphur content sank only to 0.072 pct in 20 min, but at this time was still sinking. The yield of lime here, as already stated, was over 100 pct, according to the method of calculation used, but still as high as 78 pct if all silica is assumed to be in the form of  $\text{CaSiO}_3$  instead of  $\text{Ca}_2\text{SiO}_4$ . A sulphur content in the end lime of 15.6 pct, as in this case, with a simultaneous silica con-

Table V. Data for Heats KR-30 to KR-34

| Heats                          | KR-30  |       | KR-31  |       | KR-32  |       | KR-33  |       | KR-34  |       |
|--------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|
|                                | Before | After | Before | After | Before | After | Before | After | Before | After |
| C, Pct                         | 2.91   | 2.97  | 3.08   | 3.47  | 3.26   | 3.41  | 3.16   | 3.34  | 3.18   | 3.16  |
| Si, Pct                        | 0.30   | 0.28  | 0.43   | 0.37  | 0.40   | 0.34  | 0.61   | 0.55  | 0.73   | 0.68  |
| Mn, Pct                        | 0.65   |       | 0.67   |       | 0.72   |       | 0.96   |       | 1.01   |       |
| S, Pct                         | 0.054  | 0.022 | 0.118  | 0.014 | 0.104  | 0.010 | 0.122  | 0.008 | 0.091  | 0.008 |
| Temperature, °C                | 1330   | 1255  | 1320   | 1256  | 1375   | 1332  | 1310   | 1278  | 1360   | 1296  |
| Hot metal, kg                  | 2990   |       | 2470   |       | 2410   |       | 2350   |       | 2290   |       |
| Lime powder, kg                | 240    |       |        |       |        |       |        |       |        |       |
| Coke powder, kg                | 30     |       | 40     |       |        |       |        |       |        |       |
| Total lime consumption, 240 kg |        |       |        |       |        |       |        |       |        |       |
| Total coke consumption, 70 kg  |        |       |        |       |        |       |        |       |        |       |
| Hot metal treated, 12,500 kg   |        |       |        |       |        |       |        |       |        |       |



tent of 17 pct, is an unusually high figure, which would hardly be attained in practice if the sulphur content is at the same time to be lowered to values below 0.025 pct.

At low silicon contents, the carbon as reducing agent also takes part in the reaction. At high sulphur contents an appreciable evolution of carbon monoxide can be noticed even at quite high silicon contents, such as 0.3 to 0.4 pct. This was the case, for instance, with the last described heats, KR-41 and KR-42. With lower ingoing sulphur contents, however, the silicon content must be under 0.05 pct, if the carbon is to take part in the reaction to any appreciable extent.

Figs. 8 to 10 show three heats, in which the carbon has, for the most part, taken over the role of silicon as reducing agent. It might be possible to deduce from these results that equilibrium between saturated carbon and silicon is about 0.05 pct Si at 1300°, and at 1200° about 0.02 pct.

In heat KR-40 (Fig. 10) the manganese content of the pig iron was 1.2 pct. This was maintained practically unchanged throughout the heat, which is partly shown by the low manganese content in the end lime. This reveals that the manganese content of the pig iron did not appreciably promote desulphurization, either as a reducing agent, or on account of its sulphur binding capacity.

Due to the rapid rotation of the furnace during the process, small drops of iron are formed that are mixed up in the lime charge and remain in the end lime. It is therefore advisable to allow the lime powder to pass a magnetic, dry separator after the process, by which the main part of the iron can be recovered. The grains can either be returned to the process or put back in the blast furnace, if other uses are not possible. Certain means have been found of counteracting the generation of these grains in the end lime. An addition of soda to the lime has a favorable effect in this respect. If the addition is not too great, at most about 10 pct of the amount of lime, the soda does not appear to exert any great influence on the sticking tendency of the lime charge.

In Fig. 11 the result of an experiment with an addition of soda is recorded. The rate of reaction has

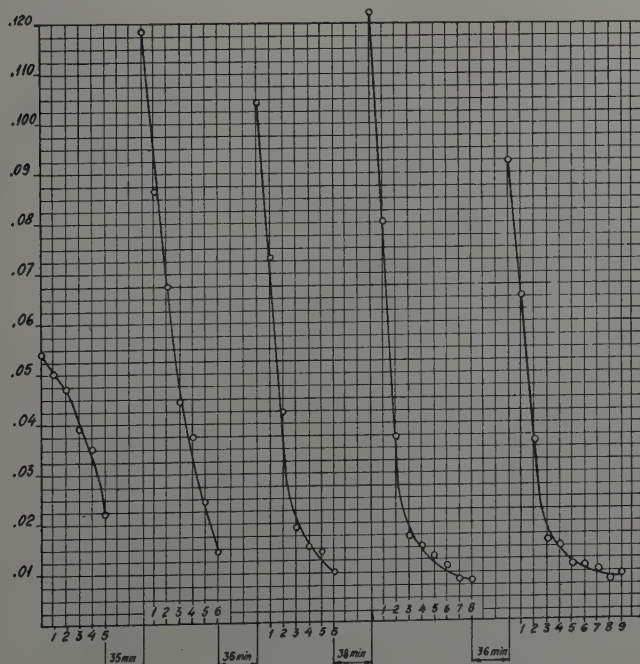
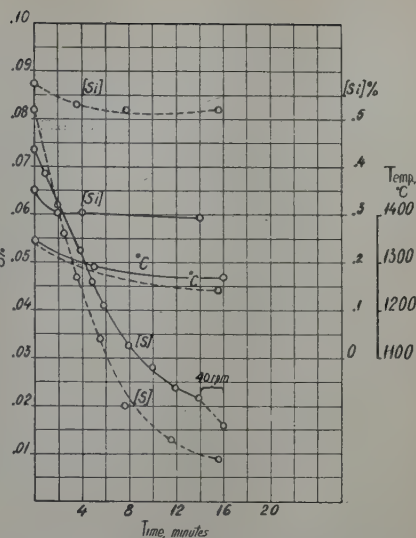


Fig. 12—Heat KR30, KR31, KR32, KR33, and KR34.

Fig. 13—Heat KR16 and KR18.

KR16 (solid line) — Hot metal, 2370 kg; C, 3.2 pct; 20 rpm. Lime powder, 38 kg; Mn, 0.5 pct. Coke powder, 19 kg; Si, 0.32 to 0.30 pct; P, 1.5 pct.  
KR18 (broken line) — Hot metal, 2500 kg; C, 2.9 pct; 40 rpm. Lime powder, 40 kg; Mn, 0.5 pct. Coke powder, 20 kg; Si, 0.57 to 0.54 pct; P, 1.8 pct.



been very slightly higher than normal, which can be ascribed to a certain catalytic influence from the soda addition. As will be seen from Table II, the sodium content in the lime charge has, however, been practically completely volatilized.

It is of course desirable from many points of view that the necessary quantity of lime be as low as possible. Even if the saving in lime is in itself of no great economic significance, a lower addition of lime has, among other things, the advantage of a smaller temperature drop in the hot metal. It seems that the amount of lime required for desulphurization of a pig iron from, for instance, 0.100 to 0.010 pct need not be expected to exceed 1 pct of the weight of the pig iron. When so small an amount of lime is used, however, the lime charge will form a thin and therefore comparatively stationary layer on the iron bath during the rotation, whereby the mixing effect may deteriorate. In order to be able to maintain a sufficiently high layer of lime in the furnace, without increasing the percentage of lime, it can be arranged so that the lime is retained in the furnace, when the hot metal is discharged, and re-employed for one or several subsequent operations. The result of an experiment along these lines is found in Fig. 12 and Table V.

Altogether 12.5 tons of pig iron was introduced in five stages, i.e., about 2.5 tons at a time. The whole amount of lime, 240 kg, was introduced at the beginning, thus corresponding to practically 10 pct of the lime present in the furnace at each treatment. Apart from the first operation, which was carried out at much too low a temperature due to the cooling effect of the large quantity of lime, in all cases the desulphurization went down to low contents very rapidly. Particularly remarkable is the rapid and complete sulphur removal even in the last experiment, although the lime in this case must, from the beginning of the treatment, have had a sulphur content of about 5 pct.

The method here described of sulphur removal in stages may be found suitable especially when very large quantities of hot metal are to be handled. Admittedly there does not appear to be any technical objection to building large furnaces, e.g., up to 100 tons capacity, but it may be preferable to employ a smaller furnace and repeat treatment several times, thus putting the lime to better use. The total treatment time need not be much longer on that account, as each part of the operation would proceed more rapidly.

As the tests have shown that desulphurization can be effected in only a few minutes, it is certainly also possible to arrange for continuous treatment by passing the hot metal at a suitable speed through a long rotating drum, in which the lime has either been placed in advance or is fed simultaneously. This procedure has been tested on small scale with promising results. Possibly an even better result can be achieved, if the lime is made to pass in counter-current to the iron by means of suitable sluice arrangements. To judge from the test results in Fig. 12, however, there does not appear to be much to be gained from employing the countercurrent principle.

The rate of rotation of the furnace can have a decisive influence on the result. In most tests 40 rpm has been used, as previously mentioned, and at this rate satisfactory results were always obtained. A few tests were made at 20 rpm, but desulphurization was not nearly so efficient.

Fig. 13 shows two heats, one at 40 rpm and the other at 20 rpm. Otherwise the treatment of the two heats was identical. At the lower rate, desulphurization proceeded far too slowly, but when the speed was increased to 40 rpm at the end of treatment, a more rapid desulphurization immediately occurred. Which rate is most suitable in different cases is hard to determine in advance, but there have been no practical difficulties whatever at the rotation speeds described. Mixing of course can be performed more efficiently by giving the furnace a form which deviates from the circular. Model experiments, for instance, have shown that the agitation effect can be greatly increased by making the furnace section slightly oval.

Finally it may be mentioned that a number of tests have been made with the addition of certain other substances to the lime charge in an attempt to improve the result still further. The addition of aluminum and calcium carbide has been tried in certain tests to increase the reducing effect. The additions resulted in a reduction of silicon to the pig iron from the furnace lining, but the desulphurization efficiency deteriorated, principally because of an increased tendency of the lime charge to form balls. Dolomite can be used as a substitute for lime, but lime is to be preferred.

The end lime obtained always has a high sulphur content, as the analyses show. The silica content has also been comparatively high in several of the tests, but if the attempt is made to avoid all unnecessary silicon oxidation and other introduction of silica, it can be kept at a low level in relation to the  $\text{CaO} + \text{CaS}$  content. The end lime should therefore be a valuable addition for sintering of iron ore, where this takes place. Most of the sulphur content then escapes in gas form.

### Summary

The method described has been carried out in a 3-ton rotating furnace at Domnarfvet Iron and Steel Works. It has the following characteristic features.

The molten iron is brought into intimate contact with powdered burnt lime by treatment in a rapidly rotating furnace.

The treatment has to take place under strongly reducing conditions, which can be made in a simple way by keeping the furnace tightly closed during the process.

The lime must be maintained in the fine powdered form during the whole treatment, which is made possible both by avoiding a temperature in excess of  $1350^{\circ}$  to  $1400^{\circ}\text{C}$  and by the addition of a suitable amount of coke powder to the lime.

By carrying out the process in this way it has been found possible to desulphurize hot metal down to very low sulphur contents in a few minutes even from relatively high starting values, and with a high lime yield.

Owing to the short time of treatment and the small lime addition necessary, the drop of temperature during the process has been very small, with the consequence that external heat supply and its associated disadvantages have been avoided.

The rotation speed normally has been the maximum of the furnace, 40 rpm. Lower speeds have also been tried, but with unsatisfactory results. No inconveniences with the high speed have been encountered.

The advantages of the method can thus be summarized as follows:

1—A very rapid and complete desulphurization can be obtained. The sulphur content can in one operation be brought down to very low values even with high starting content in the iron and with high lime yield.

2—The desulphurizing material is cheap and can be obtained everywhere. After the treatment it may be used for other purposes.

3—No formation of molten slag is taking place, with the result that attack on the lining of furnace and ladle is avoided. The furnace is of a simple construction and can advantageously be lined with ordinary fire clay.

4—The iron during the tapping can be separated easily from the lime.

5—No dangerous smoke is formed during the process.

The first plant for commercial production is in operation at Surahammar Iron and Steel Works, Surahammar, Sweden.

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# Kalling-Domnarfvet Process at Surahammar Works

by Sven Fornander

An account is given of the way in which a new process for desulphurization of hot metal is carried out at a Swedish blast-furnace plant. In the process powdered burnt lime is used as a desulphurizing agent in a rotary furnace. Results are given.

IN a paper by Kalling et al.\* the fundamentals of a new process for desulphurization of hot metal using powdered burnt lime as a desulphurizing agent were outlined. The purpose of the present paper is to give a brief account of the way in which this process is being carried out in practice by Surahammars Bruks AB, Sweden, and of the results obtained.

The hot metal from the blast furnace is tapped into a ladle of 15 tons capacity and transferred to a rotary furnace, a simplified drawing of which is given in Fig. 1. The rotary furnace has a total length of about 160 in. and an outside diameter of the rings of about 130 in. The furnace is in a horizontal position, with its rings placed on four rollers, and can be rotated by a driving mechanism at various speeds of up to 34 rpm. The rotary furnace and its driving mechanism were designed and constructed at Surahammar.

The hot metal is charged into the rotary furnace through the opening to the left in Fig. 1. See Fig. 2. An addition is then made to the furnace consisting of finely ground burnt lime amounting to 2 pct of the weight of the hot metal as well as 0.5 pct of coke breeze. After the additions are made, the furnace is sealed to the atmosphere by means of two lids and set in rotary motion at a rate of 34 rpm. The sulphur in the hot metal is rapidly absorbed by the lime added, the time of treatment needed is normally 30 min. The process is then stopped, the lid is removed, and the furnace is lifted up by a crane and used as a tilting ladle for pouring the metal into the pig-iron molds, Fig. 3.

## Process Metallurgy

The hot metal charged into the rotary furnace has a composition which usually lies within the following limits: C, 3.70 to 4.10 pct; Si, 0.80 to 1.80; Mn, 0.40 to 0.80; P, 0.025 to 0.030; and S, 0.060 to 0.200. Figs. 4 and 5 give examples of the changes in hot metal composition taking place during the treatment in the rotary furnace. As will be seen from

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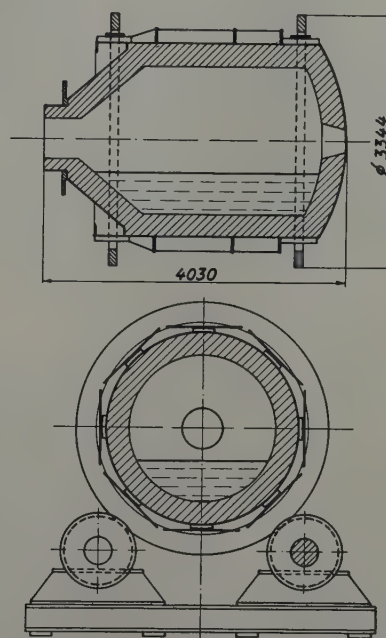
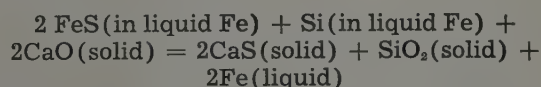


Fig. 1—Rotary furnace for desulphurization.

the diagrams, the sulphur content of the metal decreases very rapidly during the first 10 min of treatment from about 0.100 to about 0.020 pct S. During the following 20 min, the sulphur content goes down slowly to about 0.005 pct S. The carbon and silicon contents of the metal decrease by about 0.10 pct each during the treatment. The manganese and phosphorus contents remain unchanged. Thus, if the process is started with an iron of the composition given above, the finishing composition of the metal usually lies within the following limits: C, 3.60 to 4.00 pct; Si, 0.70 to 1.70; Mn, 0.40 to 0.80; P, 0.025 to 0.030; and S, 0.002 to 0.020.

The chemical reaction taking place during the process can be written:



\* B. Kalling, C. Danielsson, and O. Dragge: Desulphurization of Pig Iron with Pulverized Lime. This issue, p. 732.

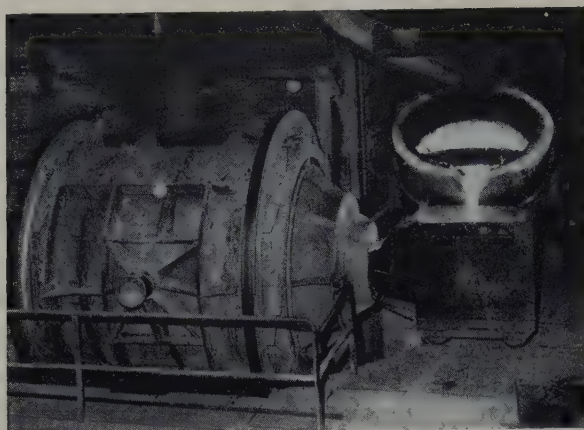


Fig. 2—Charging of the furnace.



Fig. 3—Tapping of the furnace.

The sulphur in the hot metal is absorbed by the burnt lime under formation of calcium sulphide, and the oxygen liberated from the calcium oxide combines with silicon, which is in solution in the iron, forming silica. Thus silicon is the reducing agent in the process. From the reaction formula it is obvious that the process is promoted by reducing conditions. It is quite likely that during the process the silica formed combines with lime in the form of a calcium silicate.

It may probably be said that the process is a unique one in the metallurgy of iron and steel with regard to the fact that a solid phase is reacting with a liquid metal. No liquid slag is formed during the process. After finished treatment of the iron, the "lime" (the reaction product) still is in the form of a fine powder.

The fact that the reaction takes place in the surface of contact between the solid lime and the liquid metal is of practical consequences. In order that the reaction should proceed rapidly, the surface of contact must be large. This is the reason why the lime used is in the form of a powder and also, why

a rotary furnace is required in the process. In the rotary furnace an intimate contact is brought about between the liquid metal and the solid lime. Within each of the two phases an efficient stirring action is produced.

### Factors Affecting Desulphurization

The first trials on a commercial scale with the process described above were made in May 1950 at the blast-furnace plant of Surahammars Bruks AB. In the first trials the sulphur content of the hot metal treated was not uniform from cast to cast. Since then, however, various measures have been adopted with the result that during the last few months the process has been applied continuously and given uniform results. The following factors have been found to have an influence upon the results obtained.

**Lime Character:** The lime powder used should be as pure as possible, the most harmful impurities being silica, carbon dioxide, and water. Detailed investigations on the influence of the impurities upon the desulphurization have yet not been carried out, but as rule of thumb it can be said that if the silica content of the burnt lime exceeds 5 pct, the sulphur content of the metal treated will be higher than 0.010 pct S. During the last few months of operation, the lime used has been burnt at the plant in a small and simple furnace with blast-furnace gas as a fuel. The burnt lime is stored in an air-tight container before being ground. The screen analysis of the lime powder used is given in Table I.

**Oxidation:** If good desulphurization is to be obtained, it is of particular importance that the furnace chamber is not exposed to oxidizing conditions either during the desulphurizing treatment of the metal or during the time elapsing between the treatments. During the first few months of operation, the furnace was heated between the treatments by a gas burner, which was inserted through a central opening in one end of the furnace. During this period of time, the desulphurization was incomplete and the results varied considerably. Prob-

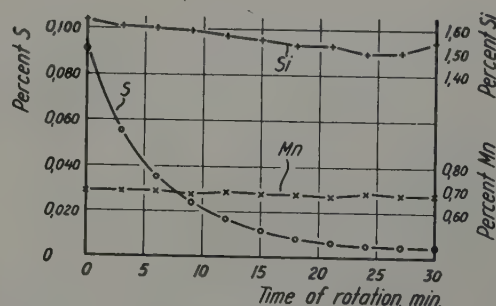


Fig. 4—Desulphurization of cast 583.

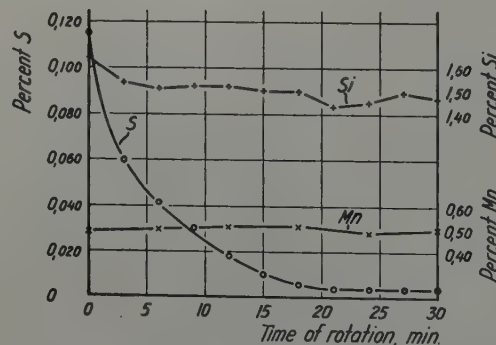


Fig. 5—Desulphurization of cast 1101.

Table I. Screen Analysis of Lime Powder

| Sieve Opening, mm | Percent |
|-------------------|---------|
| Over 1.5          | 4.0     |
| 1.5-1.0           | 2.6     |
| 1.0-0.6           | 5.4     |
| 0.6-0.3           | 5.8     |
| 0.3-0.2           | 14.3    |
| 0.2-0.1           | 19.1    |
| 0.1-0.06          | 17.4    |
| Under 0.06        | 31.4    |



ably this was due to the fact that small amounts of iron sticking to the furnace wall were oxidized by the combustion gases from the burner, the oxides formed decreasing the desulphurizing effect of the lime. However, when the furnace was sealed to the atmosphere both during the treatments and the time elapsing between them, the method gave fully satisfactory results.

If oxidizing conditions prevail in the furnace during the treatment, the lime powder forms balls when the furnace is in rotary motion. In unfavorable cases, these balls can be up to 8 in. diam. Balls will form also, if blast-furnace slag enters the furnace. The occurrence of balls is an indication of incomplete desulphurization. Difficulties of this kind have not appeared during the last few months of operation.

**Furnace Lining:** The furnace lining consists of an inside 6 in. course of ordinary fireclay bricks and two outside courses of insulating bricks having a thickness of 2½ in. each.

Table II. Results of Desulphurization of 300 Casts

| Before Treatment |              | After Treatment |              |
|------------------|--------------|-----------------|--------------|
| S, Pct           | No. of Heats | S, Pct          | No. of Heats |
| 0.020-0.050      | 51           | 0.002-0.010     | 216          |
| 0.051-0.100      | 127          | 0.011-0.020     | 60           |
| 0.101-0.150      | 87           | 0.021-0.030     | 21           |
| 0.151-0.200      | 25           | 0.031-0.040     | 3            |
| 0.201 and over   | 10           |                 |              |
| Average 0.095    | 300          | 0.009           | 300          |

After a treatment of a cast in the furnace, the inside wall is covered with a thin adhering layer, consisting of a mixture of lime powder, coke breeze, and solidified iron. The layer grows thicker with every cast treated, and when 50 or 60 casts have been treated, the layer is so thick that the furnace room is insufficient. The layer is removed by heating the furnace wall to a high temperature, about 1400°C, by means of an oil burner. However, the heating must be made with care in order to prevent the fireclay bricks from being damaged.

At present a new rotary furnace is under construction, and this unit will be provided with a basic lining. The unit will be used when the existing one is under relining.

**Hot Metal Temperature:** The temperature of the hot metal was determined at various stages of the process by means of quick-immersion thermocouples. The following figures refer to normal conditions: In blast-furnace runner, 1400°C (2550°F);

Table III. Results of Three Days' Operation

| Cast No. | Weight of Metal, Tons | S in Iron, Pct   |                 | De-sulphurization, Pct |
|----------|-----------------------|------------------|-----------------|------------------------|
|          |                       | Before Treatment | After Treatment |                        |
| 545      | 11                    | 0.068            | 0.005           | 92.7                   |
| 548      | 8                     | 0.068            | 0.003           | 95.6                   |
| 549      | 12                    | 0.068            | 0.005           | 92.7                   |
| 550      | 12                    | 0.068            | 0.011           | 83.8                   |
| 552      | 9                     | 0.091            | 0.009           | 90.1                   |
| 553      | 11                    | 0.082            | 0.009           | 89.0                   |
| 556      | 11                    | 0.105            | 0.007           | 93.4                   |
| 558      | 12                    | 0.100            | 0.005           | 95.0                   |
| 559      | 12                    | 0.100            | 0.006           | 94.0                   |
| 560      | 13                    | 0.086            | 0.005           | 94.2                   |
| 561      | 11                    | 0.086            | 0.008           | 88.4                   |
| 562      | 11                    | 0.086            | 0.004           | 95.3                   |
| 563      | 11                    | 0.077            | 0.004           | 94.8                   |
| 564      | 11                    | 0.077            | 0.004           | 94.8                   |
| 565      | 10                    | 0.070            | 0.004           | 94.3                   |
| 566      | 11                    | 0.059            | 0.008           | 86.5                   |
| 569      | 10                    | 0.100            | 0.006           | 94.0                   |
| 570      | 11                    | 0.100            | 0.005           | 95.0                   |
| 571      | 12                    | 0.096            | 0.005           | 94.2                   |
| Average  | 11                    | 0.082            | 0.006           | 92.7                   |

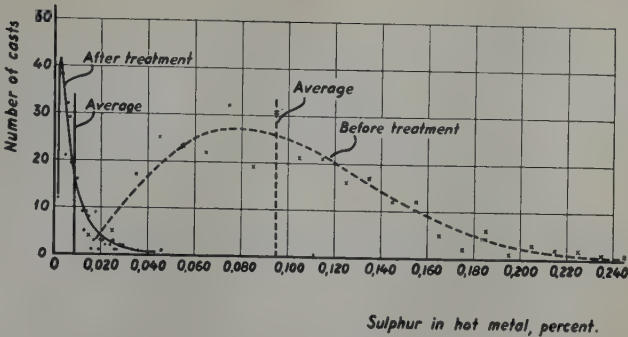


Fig. 6—Results of desulphurization of 300 casts.

in ladle when full, 1340°C (2440°F); in rotary furnace before treatment, 1320°C (2400°F); and in rotary furnace after 30 min treatment, 1250°C (2280°F).

Thus the temperature loss during the whole process amounts to about 150°C (270°F). A hot-metal temperature of 1250°C (2280°F) is sufficient for pouring the metal into the molds. However, at Surahammar's blast-furnace plant, the iron is partly used for the manufacture of ingot molds, and for this purpose a temperature of 1250°C is too low. In the near future, the hot metal will be tapped from the blast furnace directly into the rotary furnace. This procedure will probably reduce the temperature loss to 70° or 80°C, and it is intended to use the hot metal treated in the rotary furnace in the ingot mold foundry. Variations in the temperature of the hot metal seem to have no influence upon the desulphurization obtained.

Results Obtained

In order to illustrate the desulphurizing effect that can be expected if the process is used in practice, a collection has been made of the results obtained in the treatment of the last 300 casts from the blast furnace, Table II and Fig. 6.

As will be seen from the table the majority of the casts (249 out of 300) had a sulphur content before treatment of 0.051 pct S or more. The sulphur content in the casts treated was 0.010 pct S or less in 216 cases and 0.020 pct S or less in 276 cases.

The average sulphur content of the iron cast from the blast furnace was 0.095 pct S during the period in question. The average sulphur content of the iron treated in the rotary furnace was 0.009 pct S. This implies that on an average 90.5 pct of the sulphur in the hot metal was removed in the rotary furnace.

Table III shows results of three days' operation. The values confirm that the desulphurizing process described above is an effective one.

Summary

An account is given of the results obtained by Surahammars Bruks AB, Sweden, with a new process for desulphurization of hot metal from a blast furnace. In the process the hot metal is treated with finely ground powder of burnt lime in a rotary furnace. About 90 pct of the sulphur in the metal is removed in the process, which after some months of experience has been found simple and inexpensive in operation.

Acknowledgments

The author is indebted to Einar Ameén, Managing Director, and Yngve Törneman, Technical Director, of Surahammars Bruks AB, for their kind permission to publish the results presented in this paper.

# A Corrected CO/CO<sub>2</sub> Ratio for Blast Furnaces

by Sid T. Killian

The utilization of the reducing power of blast-furnace gas can be estimated by applying two rectifying calculations to the gas analysis. A resulting corrected CO/CO<sub>2</sub> ratio varies inversely with furnace production. Directions for calculating the corrected CO/CO<sub>2</sub> ratio are given, and a corrected CO/CO<sub>2</sub> ratio is compared with actual furnace production.

THE inadequacy of the normally accepted CO/CO<sub>2</sub> ratio as a measure of blast-furnace performance and furnace efficiency was discussed following the presentation of the paper by H. F. Dobscha.\* In this outstanding example of careful observation on large scale blast-furnace operation, the changes occurring with beneficiated ores were: 1—A net gain in tonnage of 21.2 pct. 2—A decrease in net coke of 15.3 pct. 3—A decrease of 1.9 pct in the CO/CO<sub>2</sub> ratio. In this great change in furnace performance, the CO/CO<sub>2</sub> ratio proved itself worthless.

The discussion of the inadequacy of expressing furnace performance and efficiency by the CO/CO<sub>2</sub> ratio led indirectly to the calculations forming the basis of this paper. At that time Dr. T. L. Joseph said: "We must consider difference in CO<sub>2</sub> from the stone in the two cases when we talk about the ratios

of CO/CO<sub>2</sub>." This statement is used for the second of the two CO/CO<sub>2</sub> ratio corrections forming the basis of this paper.

The research work in attempting to find out why the furnaces could operate so differently with practically the same CO/CO<sub>2</sub> ratio lead not to the answer sought but, after a shift to the gaseous phase in the research work, the proof that the normal CO/CO<sub>2</sub> ratio was outmoded and a new corrected ratio should replace it. To be of any value, any new corrected ratio should express approximate furnace efficiency and give an idea of practical furnace performance to be expected. This the normal CO/CO<sub>2</sub> ratio has failed to do. However, in the absence of anything better, some credence has been attached to the normal CO/CO<sub>2</sub> ratio. As far as the writer can ascertain, the present paper is the first attempt to change or improve the normally accepted index of

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\* H. F. Dobscha: Effect of Sized and Sintered Mesabi Iron Ores on Blast-furnace Performance. *Proc. Blast Furnace, Coke Oven and Raw Materials Committee, AIME* (1948) 7, p. 49.



Table I. Various Gas Analyses with One Corrected Ratio

|                         |       |        |        |        |        |        |        |
|-------------------------|-------|--------|--------|--------|--------|--------|--------|
| Volume CO               | 29.50 | 29.00  | 28.50  | 28.00  | 27.50  | 27.00  | 26.50  |
| Volume CO <sub>2</sub>  | 11.00 | 11.50  | 12.00  | 12.50  | 13.00  | 13.50  | 14.00  |
| Volume H <sub>2</sub>   | 00.00 | 00.50  | 01.00  | 01.50  | 02.00  | 02.50  | 03.00  |
| Volume N <sub>2</sub>   | 57.50 | 57.50  | 57.50  | 57.50  | 57.50  | 57.50  | 57.50  |
| Volume Total            | 98.00 | 98.50  | 99.00  | 99.50  | 100.00 | 100.50 | 101.00 |
| Percent CO              | 30.10 | 29.44  | 28.79  | 28.14  | 27.50  | 26.87  | 26.24  |
| Percent CO <sub>2</sub> | 11.22 | 11.68  | 12.12  | 12.56  | 13.00  | 13.43  | 13.86  |
| Percent H <sub>2</sub>  | 0.00  | 0.51   | 1.01   | 1.51   | 2.00   | 2.49   | 2.97   |
| Percent N <sub>2</sub>  | 58.67 | 58.38  | 58.08  | 57.79  | 57.50  | 57.21  | 56.93  |
| Percent Total           | 99.99 | 100.01 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| CO ratio                | 30.10 | 29.44  | 28.79  | 28.14  | 27.50  | 26.87  | 26.24  |
| CO <sub>2</sub>         | 11.22 | 11.68  | 12.12  | 12.56  | 13.00  | 13.43  | 13.86  |
| Ratio                   | 2.683 | 2.521  | 2.375  | 2.240  | 2.115  | 1.994  | 1.893  |

furnace efficiency. A corrected CO/CO<sub>2</sub> ratio is proposed as the future criterion of the blast furnace.

### Corrections Necessary

The calculations involved in figuring the corrected CO/CO<sub>2</sub> ratio are performed in two main steps. The first calculation involves placing the gas analysis on a hydrogen-free basis. The second calculation consists of deducting the amount of CO<sub>2</sub> evolved by the flux from the gas analysis.

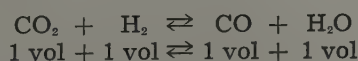
The first correction is almost mandatory, if the CO/CO<sub>2</sub> ratio is to be continued as a measure of furnace efficiency, inasmuch as it can be figured so easily. The second step however should be adapted to furnace records and must be used carefully to render true service.

When the gas analysis is placed on a hydrogen-free basis, the CO/CO<sub>2</sub> ratio expresses the ratio of the total unused reducing power to the used reducing power with the flux CO<sub>2</sub> included as used reducing power. The normal CO/CO<sub>2</sub> ratio attempted to give a ratio of unused to used reducing power, but the resulting ratio could vary considerably due to the exclusion of the hydrogen content of the gas and the inclusion of the flux CO<sub>2</sub> in the ratio. However when both corrections are made, a close expression of the ratio of unused reducing power to used reducing power in the gaseous phase is obtained. Neither correction should be omitted if any resulting corrected CO/CO<sub>2</sub> ratio is to be used as a representation of furnace efficiency or furnace performance.

### Chemical Principles of the First Correction

*Gas Analysis on a Hydrogen-Free Basis:* The gas-analysis correction of placing the gas analysis on a hydrogen-free basis in no way involves furnace reactions, but merely corrects the gas analysis for a variable which can change the actual gas analysis and the ratio calculated from it.

The equation:



shows how the interaction of the CO<sub>2</sub> and the H<sub>2</sub> with the CO and the H<sub>2</sub>O can change the ratio. As the H<sub>2</sub> increases, the CO<sub>2</sub> is increased at the expense of and in the same amount as the CO is decreased. Similarly, as the H<sub>2</sub> decreases, the CO<sub>2</sub> is decreased in the same amount as the CO is increased. The variable of the hydrogen content of the gas is eliminated by changing the gas analysis so that the reaction goes to completion in the direction that eliminates the hydrogen. The two components of the CO/CO<sub>2</sub> ratio are then left for the calculation. Thus the correction merely involves the subtraction of the percentage of hydrogen in the gas from the percentage of carbon

dioxide in the gas and the simultaneous addition of the percentage of hydrogen in the gas to the percentage of carbon monoxide in the gas. In other words, every 1 pct of H<sub>2</sub> in the gas analysis will drop the CO<sub>2</sub> percentage exactly 1 pct and simultaneously raise the CO percentage exactly 1 pct when the correction is made.

In order to show clearly how the hydrogen content of the gas changes the normal CO/CO<sub>2</sub> ratio, Table I has been calculated. In it all volumes are changed entirely by the reaction:



in steps of 0.50 volumes of each of the reacting gases. All the analyses and CO<sub>2</sub> ratios in Table I are identical when placed on the hydrogen-free basis. All given an identical corrected ratio of 2.683.

### Second Correction

*Gas Analysis with Flux CO<sub>2</sub> Deducted:* While the CO<sub>2</sub> evolved from the stone is an important factor in furnace performance and furnace efficiency, from an overall viewpoint, the calcining of the stone consists of the addition of CO<sub>2</sub> (completely oxidized carbon) to the gaseous phase. The inclusion of this CO<sub>2</sub> tends to give an illusion that a greater oxidation of carbon is taking place than really occurs. In other words, the inclusion of this CO<sub>2</sub> tends to hide the real efficiency.

The second correction of taking the gas analysis on a hydrogen-free basis and deducting the CO<sub>2</sub> evolved from the flux is best accomplished by equating the total carbon input with the total carbon output. The easiest means of computing this carbon balance should be to use 24 hr as the basis with no calculations involving the wind blown. The blowing media used vary widely in efficiency and quite often the wind ordered differs markedly from the actual wind delivered. Thus complex stoichiometric calculations are avoided and practically all calculations can be made from furnace records.

*Carbon Balance:* The carbon input normally includes: 1—net coke carbon to furnace excluding fractions not charged, 2—carbon in stone, and 3—carbon in scrap. The carbon output normally includes: 1—CO in gas, 2—CO<sub>2</sub> in gas, 3—carbon in total amount of pig iron produced, 4—carbon in flue dust and sludge, 5—coke messes, 6—rolls and slips, 7—carbon in the gas as coke particles and as stone particles, and 8—hydrocarbons in the gas.

All the items should be observed and calculated before assuming them to be negligible. For a complete carbon balance, every item should be checked.

*Illustration of Calculation:* The corrected CO/CO<sub>2</sub> ratio is illustrated in the calculation of a furnace using 1.00 fuel (80 pct net carbon) with 300 lb of

Table II. Calculation of Corrected CO/CO<sub>2</sub> Ratio

|                                                                 |       |
|-----------------------------------------------------------------|-------|
| <b>Input</b>                                                    |       |
| Coke, net lb carbon per ton pig.....                            | 1600. |
| Stone, net lb carbon per ton pig.....                           | 100.  |
| Input, net lb carbon per ton pig.....                           | 1700. |
| <b>Output</b>                                                   |       |
| Pig iron, net lb carbon (4.2 pct).....                          | 84.   |
| Flue dust, net lb carbon.....                                   | 30.   |
| Gas, net lb carbon by difference.....                           | 1586. |
| Output, net lb carbon per ton pig.....                          | 1700. |
| Fraction carbon in gas from flux = 100/1586 = 0.0631            |       |
| In gas analysis from flux = (30.10 + 11.22) × 0.0631 = 2.61 pct |       |
| In gas analysis not from flux = 11.22 — 2.61 = 8.61 pct         |       |
| In gas from furnace reactions = 8.61 pct                        |       |

Table III. Blast Furnace Performance

| Ores Used                             | Normal | Beneficiated | Difference, Pct |
|---------------------------------------|--------|--------------|-----------------|
| Iron production, net tons per day     | 1324   | 1605         | +21.2           |
| Coke, net lb per ton                  | 1782   | 1510         | -15.3           |
| Flue dust and sludge, lb per ton      | 284    | 227          | -20.1           |
| Silicon in iron                       | 0.91   | 0.87         |                 |
| Sulphur in iron                       | 0.030  | 0.030        |                 |
| Wind blown, cfm at 60°F and 30 in. Hg | 83,604 | 85,651       | + 2.4           |
| Moisture in blast, grains per cu ft   | 2.3    | 2.3          |                 |
| Analysis of top gases, pct            |        |              |                 |
| CO                                    | 26.57  | 26.17        |                 |
| CO <sub>2</sub>                       | 12.33  | 12.40        |                 |
| H <sub>2</sub>                        | 2.30   | 1.60         |                 |
| CH <sub>4</sub>                       | 0.13   | 0.13         |                 |
| N <sub>2</sub>                        | 58.67  | 59.70        |                 |
| Ratio CO/CO <sub>2</sub>              | 2.15   | 2.11         |                 |

flue dust (10 pct carbon). Carbon in the flux is taken at 100 lb per ton of pig iron. The gas analysis equating the various CO/CO<sub>2</sub> ratios to a hydrogen-free basis is used for this calculation, Table II.

Thus with the gas analysis illustrated and containing 2.00 pct hydrogen, the normal CO/CO<sub>2</sub> ratio is 2.115. The CO/CO<sub>2</sub> ratio on a hydrogen-free basis is 2.683. The corrected CO/CO<sub>2</sub> ratio on a hydrogen-free basis with the correction for the CO<sub>2</sub> evolved from the flux is 3.496.

#### Comparison of Corrected CO/CO<sub>2</sub> Ratio with Furnace Performance

The method involved in calculating the corrected CO/CO<sub>2</sub> ratio from the Dobscha-United States Steel furnaces differs markedly from the preceding calculations, which are given as the method to be used normally. In the following calculations, the corrected CO/CO<sub>2</sub> ratio is calculated from the carbon distribution in the gas, since complete figures for calculating by the carbon-balance method were not included in the paper. Then the old ratio and the corrected CO/CO<sub>2</sub> ratio are compared with the furnace production. In other words, the old and the corrected CO/CO<sub>2</sub> ratios are being checked against the performance of the Dobscha-United States Steel furnaces.

For the benefit of any who have not read Dobscha's paper,\* the following is taken directly from it: "A program was carried out involving two modern identical blast furnaces with a hearth diameter of

Table IV. Carbon in Top Gases per Ton Iron

|                                                                 | Normal Ores      | Beneficiated Ores |
|-----------------------------------------------------------------|------------------|-------------------|
| Carbon in CO, lb                                                | 1024             | 838               |
| Carbon in total CO <sub>2</sub> , lb                            | 475              | 397               |
| Carbon in flux CO <sub>2</sub> , lb                             | 113              | 76                |
| Fraction of total carbon in the gas evolved from the flux       | 113/(1024 + 475) | 76/(838 + 397)    |
| Percentage of the total carbon in the gas evolved from the flux | 7.54             | 6.15              |

Table V. Percentage CO<sub>2</sub> from Flux

| Gas Analysis, Hydrogen Free      | Normal Ores | Beneficiated Ores |
|----------------------------------|-------------|-------------------|
| CO in gas, pct                   | 28.87       | 27.76             |
| CO <sub>2</sub> in gas, pct      | +10.03      | +10.80            |
| Total CO + CO <sub>2</sub> , pct | 38.90       | 38.56             |
|                                  | × 0.0754    | × 0.0615          |
| CO <sub>2</sub> from flux, pct   | 2.93        | 2.37              |

27 ft 6 in. A mixture of beneficiated ores was charged on one furnace for a continuous period of one month and normal ores charged on the other furnace. During an interim period of one month, the burdens were reversed and the test was continued for a two-month period. Coke, flux, and miscellaneous burdening materials were of the same quality on both furnaces; the quantities of the latter being identical except for deviations dictated by operating practice." Table III is taken from p. 55 of the 1948 *Proceedings of the Blast Furnace, Coke Oven and Raw Materials Committee, AIME*.

#### Gas Ratio Calculated to a Hydrogen-Free Basis

The gas ratio calculated to a hydrogen-free basis follows:

| Normal Ores  | Beneficiated Ores |
|--------------|-------------------|
| 26.57 + 2.30 | 26.17 + 1.60      |
| 12.33 - 2.30 | 12.40 - 1.60      |
| 28.87        | 27.76             |
| 10.03        | 10.80             |
| 2.878        | 2.562             |

#### Corrections for Flux CO<sub>2</sub> in Gas Analysis

The second correction in calculating the corrected CO/CO<sub>2</sub> ratio is to deduct the CO<sub>2</sub> evolved by the flux from the total CO<sub>2</sub> in the gas analysis on a hydrogen-free basis. In this case it is performed in three steps. 1—The fraction or percentage of total gas carbon which comes from the flux carbonate is calculated. 2—This fraction or percentage then is expressed as percentage CO<sub>2</sub> in the gas analysis. 3—The percentage CO<sub>2</sub> from the flux is subtracted from the CO<sub>2</sub> in the gas on a hydrogen-free basis. The corrected CO/CO<sub>2</sub> ratio can then be calculated.

*Percentage of Total Gas Carbon from Flux Carbonates:* The first step in tying in the CO<sub>2</sub> from the flux with the CO<sub>2</sub> in the gas analysis is to calculate the percentage of the carbon in the gas which comes from the flux. The figures for that calculation follow.

The carbon distribution in the top gases in Dobscha's furnaces is given in Table IV.

*Gas Analysis Percentage of CO<sub>2</sub> from Flux Carbonate:* The second step in tying in the CO<sub>2</sub> from the flux with the CO<sub>2</sub> in the gas analysis is to find the percentage of CO<sub>2</sub> which came from the flux expressed in gas analysis percentage. This calculation

Table VI. Correction of Gas Analysis for CO<sub>2</sub> from Flux

| Gas Analysis, Hydrogen Free                 | Normal Ores | Beneficiated Ores |
|---------------------------------------------|-------------|-------------------|
| CO <sub>2</sub> in gas, pct                 | 10.03       | 10.80             |
| CO <sub>2</sub> from flux, pct              | -2.93       | -2.37             |
| CO <sub>2</sub> from furnace reactions, pct | 7.10        | 8.43              |

Table VII. CO/CO<sub>2</sub> Ratio vs. Production

|                                                                                 | Normal Ores | Beneficiated Ores | Comparative Ratio |
|---------------------------------------------------------------------------------|-------------|-------------------|-------------------|
| Production, tons pig iron                                                       | 1324        | 1605              | 0.8249            |
| CO/CO <sub>2</sub> ratio, regular gas analysis                                  | 2.1549      | 2.1105            | 1.021             |
| CO/CO <sub>2</sub> ratio, corrected for H <sub>2</sub>                          | 2.878       | 2.562             | 1.123             |
| CO/CO <sub>2</sub> ratio, corrected for H <sub>2</sub> and flux CO <sub>2</sub> | 4.066       | 3.293             | 1.235             |
| Inverse ratio of pig iron production                                            |             |                   | 1.212             |



is given in Table V. These figures show the direct amount in gas analysis percentages of  $\text{CO}_2$  evolved from the flux. In other words, these calculated percentages of  $\text{CO}_2$  are to be deducted from the total percentage of  $\text{CO}_2$  on a hydrogen-free basis.

*Gas Analysis Correction for  $\text{CO}_2$  Evolved from Flux:* The calculations correcting the gas analysis on a hydrogen-free basis for the  $\text{CO}_2$  evolved from the flux is given in Table VI.

The corrected  $\text{CO}/\text{CO}_2$  ratio then is:

|       |       |
|-------|-------|
| 28.87 | 27.76 |
| 7.10  | 8.43  |
| 4.066 | 3.293 |

The above figures show the corrected  $\text{CO}/\text{CO}_2$  ratio calculated on a hydrogen-free basis with the correction for the  $\text{CO}_2$  evolved from the flux.

The ratios 1.235 and 1.212 in Table VII show how closely the ratio of the corrected  $\text{CO}/\text{CO}_2$  ratios compares with the ratio of iron production in an inverse manner. Mathematically:

$$\text{Production} \times \text{Corrected Ratio} = \text{A Constant}$$

As shown in Table VIII, the product of the corrected  $\text{CO}/\text{CO}_2$  ratio and the iron production differ by approximately 2 pct when the normal and beneficiated ores are compared. In other words, the product of the corrected  $\text{CO}/\text{CO}_2$  ratio and the iron production should approximate a constant when similar furnaces are compared or when conditions are changed on the same furnace.

This constant might be one of the benefits of the corrected  $\text{CO}/\text{CO}_2$  ratio as a tool of production. However, the constant might not be a straight-line function of the inverse production and checking should be done before it can be accepted as such. For normal changes on one furnace, the variation from a straight line would be negligible. At this time, the constant is used only to illustrate the close tie-in of the corrected  $\text{CO}/\text{CO}_2$  ratio with the corresponding furnace production.

### Summary and Conclusions

1—A corrected  $\text{CO}/\text{CO}_2$  ratio is proposed as an index of blast-furnace performance. It is the  $\text{CO}/\text{CO}_2$  ratio of the blast-furnace gas on a hydrogen-free basis with the flux  $\text{CO}_2$  deducted from the gas analysis. On iron of similar analysis, it gives a closer expression of the efficacy of the gasified carbon of the fuel in removing the oxygen from the ore.

2—The calculations involved in figuring the corrected  $\text{CO}/\text{CO}_2$  ratio should be as accurate as possible. Since the answer is in the form of a ratio, the methods used in obtaining all figures should be the same in all cases. They should not vary unless the same answer is obtained.

3—The corrected  $\text{CO}/\text{CO}_2$  ratio probably will show changes in furnace performance quicker than any other method available. Given similar conditions of furnace performance, a 24-hr lapse should show whether any change is or is not beneficial. One decided advantage is that a satisfactory comparison can be made on a furnace when changing ore, fuel, flux, slag volume, moisture in the wind, products, or any variable affecting furnace performance such as filling, shape of combustion zone, or top pressure. In short, factors changing furnace performance can be correlated quicker and better due to the more accurate ratio used for comparison.

4—If large changes are made in iron analysis, addi-

Table VIII. Comparison of Normal and Beneficiated Ores

|                    | Normal Ores  | Beneficiated Ores |
|--------------------|--------------|-------------------|
| Product            | 1324 x 4.066 | 1605 x 3.293      |
| Product            | 5384.4       | 5285.3            |
| Average            |              | 5334.9            |
| Difference         |              | 99.1              |
| Difference/Average |              | 1.84%             |

The above product of the corrected  $\text{CO}/\text{CO}_2$  ratios and the iron production approximate a constant with a swing of 1.84 pct.

|                    |               |               |
|--------------------|---------------|---------------|
| Product            | 1324 x 2.1549 | 1605 x 2.1105 |
| Product            | 2853.1        | 3387.4        |
| Average            |               | 3120.3        |
| Difference         |               | 534.3         |
| Difference/Average |               | 17.12%        |

The above product of the normal  $\text{CO}/\text{CO}_2$  ratios and the iron production approximate a constant with a swing of 17.12 pct.

tional corrections might be necessary to allow for oxygen removed from reduced elements entering the iron. A distinct possibility exists that with due allowance for heats of reaction, almost all furnace products could be placed on a comparable basis.

5—No attempt has been made to introduce too many additional corrections at this time. Subsequent evaluation of the Killian-Joseph corrections should suggest them if needed. For instance the oxygen evolved from the metalloids has not been considered. It is felt that this paper covers sufficient territory at this time.

6—Attention is again called to the fact that the basis for the second correction was first proposed by Dr. T. L. Joseph in his discussion on why the normal  $\text{CO}/\text{CO}_2$  ratio failed.

7—The corrected  $\text{CO}/\text{CO}_2$  ratio as here applied to the furnace performance used, deviates 1.84 pct from being an accurate ratio, compared with a deviation of 17.12 pct with the normal ratio. In the instance used, the corrected  $\text{CO}/\text{CO}_2$  ratio shows one-ninth the divergence of the normal ratio if applied directly to furnace production. Roughly speaking it is nine times as accurate.

8—Attention is again called to the fact that the normal  $\text{CO}/\text{CO}_2$  ratio changed from 2.15 to 2.11 in going from normal to beneficiated ores, while the corrected  $\text{CO}/\text{CO}_2$  ratio changed from 4.066 to 3.293. Thus the normal  $\text{CO}/\text{CO}_2$  ratio was not only worthless, but in this specific case must be considered as definitely misleading. While the normal  $\text{CO}/\text{CO}_2$  ratio tends to hide it, the corrected  $\text{CO}/\text{CO}_2$  ratio expresses the change in the reducing power of the gas which has been utilized by the furnace.

9—In order to have the second portion of this work presented in as clear form as possible, the 0.13 pct  $\text{CH}_4$  in the furnace gases from the normal and beneficiated ores has been omitted from the calculations. A correction similar to, but more complicated than, placing the gas on a hydrogen-free basis would have been necessary. Thus every volume of  $\text{CH}_4$  in the gas would require the deduction of three volumes of  $\text{CO}_2$  and the simultaneous addition of four volumes of  $\text{CO}$  when the correction is made. With 0.13 pct  $\text{CH}_4$  in both gases, this correction was omitted.

10—The corrected  $\text{CO}/\text{CO}_2$  ratio is not a perfect comparison of the working of a furnace and must not be considered as such. It is presented as the simplest and most practical numerical expression of the efficiency of the blast furnace in terms of relative efficiency and relative production.

# Burst Phenomenon in the Martensitic Transformation

by E. S. Machlin and Morris Cohen

The martensite reaction in single crystals and polycrystals of 70 pct Fe-30 pct Ni alloys is shown to be autocatalytic in nature, producing bursts of transformation during cooling. The temperature of the first burst of transformation, called  $M_b$ , occurs below  $M_s$  in these alloys. Experiments were devised to test the athermal embryo and strain embryo theories of martensite nucleation. The results indicate that internal strains, either within the virgin austenite or around existing martensitic plates, control the nucleation process in these alloys. Furthermore, the growth of martensitic plates is not limited by the attainment of an elastic balance with the austenitic matrix, but by the occurrence of plastic deformation at the martensite boundaries which interferes with the propagation mechanism.

IN an investigation of the martensitic habit in single crystals of a 69 pct Fe-31 pct Ni alloy,<sup>1</sup> it was observed that about 25 pct of the austenite transformed during subatmospheric cooling within the time-interval of an audible click. This event proved quite spectacular: The shock wave sent out from the specimen freely suspended on a thread in the refrigerating liquid was occasionally sufficiently intense to shatter the Dewar container and to separate the toluene column in the immersed thermometer. The present investigation was undertaken to determine the kinetics and mechanism of this "burst" type of martensitic reaction.

The analyses of the alloys studied are given in Table I. The composition of the single crystal specimens is designated by alloy A, while the polycrystalline specimens were made of alloys B and C as noted in the text. The single crystals were prepared in a vacuum furnace, using a modified Bridgman technique. Most of these crystals were homogenized by holding for 24 hr at about 1300°C just after solidification. However, it may be emphasized here that the degree of homogenization was not a controlling factor in the subsequent experiments, inasmuch as specimens having different degrees of homogenization yielded the same results. All of the single crystals were fully austenitic as slowly cooled to room temperature.

An illustration of the burst phenomenon is given in Fig. 1, which shows oscillograms of electrical resistivity and temperature vs. time during the continuous quenching of 1/16 in. wire specimens (alloy B) in a dry ice and acetone bath at -77°C. There are at least two observable bursts in this case, as indicated by the sharp decreases of resistance accompanying the sudden formation of substantial quantities of martensite. The thermal arrest during the quench probably corresponds to the larger burst. Usually the bursts are followed by more or less progressive transformation during continuous cooling.

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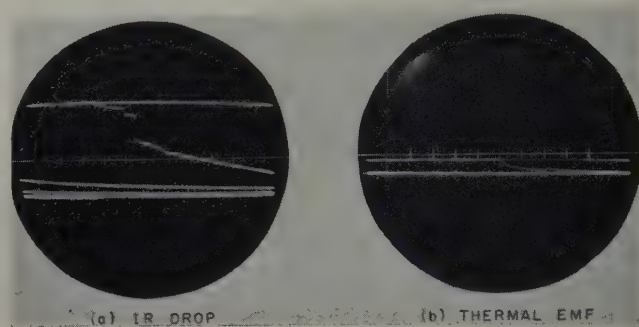


Fig. 1—Oscillographs recorded during quench of a 70.5 pct Fe-29.5 pct Ni alloy into a  $\text{CO}_2$  and acetone bath at -77°C. Each horizontal interval corresponds to 0.1 sec. a—Change in resistivity of specimen. b—Change in temperature of specimen. In each case, top line corresponds to +25°C, bottom line corresponds to -77°C.

It will also be noted that the resistance continues to decrease after the specimen has reached the bath temperature. This isothermal change denotes the formation of martensite at constant temperature, and will be the subject of another paper.

Examination of fiducial scratches on the surface of a transformed single crystal has shown<sup>2</sup> that the scratches in adjoining nonparallel martensitic plates are usually bent in opposite directions, as though one plate forms in such a way as to relieve the matrix stresses set up by the adjacent plate. This, together with some of the results described in ref. 1,

Table I. Compositions of Alloys Studied, in Percent

| Alloy | Ni       | C     | N     | Mn    | Si   | P     | S     | Cr   |
|-------|----------|-------|-------|-------|------|-------|-------|------|
| A     | 31±0.3   | 0.048 | 0.027 | 0.003 | 0.56 | 0.007 | 0.002 |      |
| B     | 29.5±0.2 | 0.036 | 0.02  | 0.19  | 0.09 | 0.008 | 0.006 |      |
| C     | 19.99    | 0.52  |       | 0.37  | 0.47 | 0.010 | 0.015 | 0.04 |

led to the tentative concept that a cooperative action exists which provides the impetus for much of the transformation that appears during the burst. The following series of experiments were performed in order to test this idea.

## Cooperative Nature of the Burst

Two adjacent disks, 1/8 in. thick x 3/4 in. diam, were cut from a single austenite crystal of alloy A using a jeweler's saw. One of the disks was then cut into 15 parts. Then 12 of the latter pieces and the second disk were austenitized (stress relieved) at 600°C for 30 min and water quenched to room temperature. The temperatures at which the first burst of transformation appeared were determined for



each specimen by cooling below room temperature. The temperature of the first burst of transformation has been termed  $M_b$  to distinguish it from the well-known  $M_s$  temperature, where the first plates of martensite form. The results given in Table II show that  $M_b$  varied from  $-54^\circ$  to  $-78^\circ\text{C}^*$  and that the whole disk transformed within  $2^\circ$  of the highest burst temperature found for the separate parts. Furthermore, the amount of martensite produced at  $M_b$  in the disk and in each of the individual pieces was of the order of 20 to 30 pct. Before examining the significance of these findings, another series of experiments that yielded similar results will be described.

Martensite range curves were determined for bulk specimens of polycrystalline alloys B and C as well as for powders (200 mesh) comprised of filings from these alloys. The purpose of subdividing the polycrystalline specimens into powders was the same as for the single crystal experiments, namely, to eliminate the cooperative effect, if such existed, and to reveal the distribution of transformation among the individual polycrystalline particles. This principle has already been applied to a study of solidification of liquids by Turnbull.<sup>3</sup>

The procedure involved in obtaining the range-curve data was as follows: The specimens were sealed in evacuated Vycor tubes, then austenitized at  $1200^\circ\text{C}$  for 1 hr, quenched in water to room temperature (after which the tubes were broken), and finally cooled to a sequence of subzero temperatures in the martensite range. The amounts of martensite in both the massive and powdered specimens were determined by lineal analysis.<sup>4</sup>

Results for alloy C\*\* are given in Fig. 2. Alloy B yielded similar effects. The range curve for the bulk polycrystalline specimens exhibits a sharp increase in transformation at  $M_b$ , followed by an increase in the amount of transformation (possibly stepwise) with decreasing temperature. The range curve for the powdered samples discloses a gradual increase in amount of transformation with decreasing temperature, without the initial sudden jump found for the bulk specimens. Thus, the subdivision effect re-

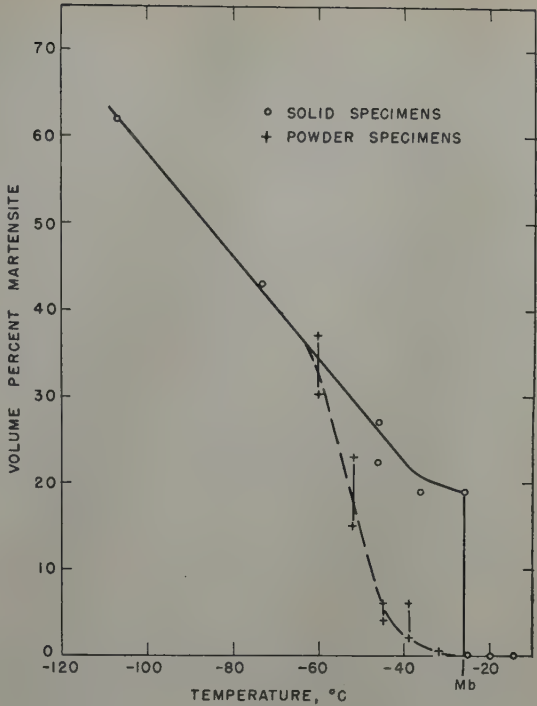


Fig. 2—Martensite range curves of bulk and powdered polycrystalline specimens of 79.5 pct Fe-20 pct Ni-0.5 pct C alloy.

ported in Table II for the single crystals is also displayed by the polycrystalline specimens: That is, not all the powder transformed the same amount at the same temperature, but instead there were particles that burst at different temperatures. The number of particles that burst increased with decreasing temperature, until all the particles had undergone a burst.

It was found that the physical subdivision of the whole into parts resulted in less total transformation and a smaller number of martensitic plates, at a given temperature, than would have been obtained for the unseparated whole. The separation eliminates the elastic coupling between the isolated parts, so that no stresses are transmitted from one part to another. Hence, it may be concluded that a cooperative effect exists in the phenomenon of the burst. The formation of a small number of plates, presumably beyond some critical amount or in some critical way, appears to catalyze the further transformation which occurs cataclysmically as a burst in less than  $10^{-4}$  sec.<sup>5</sup>

The burst phenomenon cannot be explained either by the existence of a large number of embryos that are slightly subcritical just above the burst temperature, in accordance with the athermal nucleation concept of Fisher, Hollomon and Turnbull,<sup>6</sup> or by the sudden isothermal formation of a large number of embryos at the burst temperature, in accordance with the thermal nucleation concept of Kurdjumow.<sup>7</sup> This is deduced from the fact that very few of the subdivided parts of the crystals or powders of polycrystals undergo the burst at the same temperature. If it should be argued that the temperature variation of the burst was caused by the samples being too small to be representative and/or that the nickel

Table II. Effect of Subdividing Single Crystals of 69 Fe-31 Ni Alloy upon Martensite Burst Temperature

All specimens were austenitized at 600°C after being cut to size.

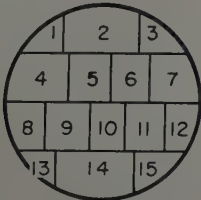
**Specimen**  
Single crystal disk (1/8 in. thick  
× 1/2 in. diam)

$M_b$ , °C  
—56

---

**Position from Single Crystal Disk**

|        |       |
|--------|-------|
| No. 1  | —54   |
| No. 11 | —56   |
| No. 2  | —62   |
| No. 4  | —68.4 |
| No. 8  | —70   |
| No. 15 | —71.5 |
| No. 12 | —76.5 |
| No. 7  | —77.5 |
| No. 14 | —77.5 |
| No. 5  | —78   |
| No. 6  | —78   |
| No. 9  | —78   |



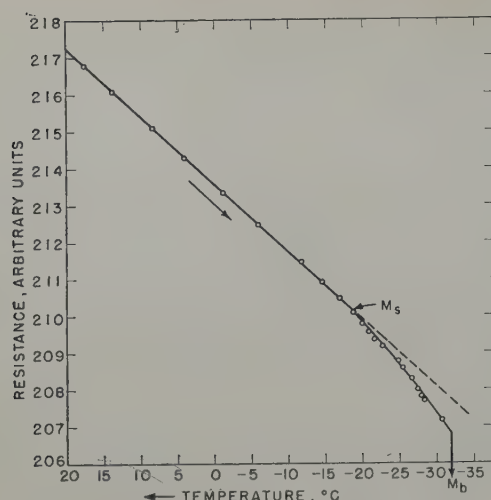


Fig. 3—Electrical resistance as a function of temperature during subcooling of polycrystalline 70.5 pct Fe-29.5 pct Ni alloy.

content of the alloy varied from part to part, these alternatives may be ruled out by the following:

1—The samples in the single crystal experiments were at least  $\frac{1}{8} \times \frac{1}{8} \times \frac{1}{8}$  in. and hence should have been large enough to contain a representative distribution of embryos. Also the martensitic plates formed therein were not perceptibly controlled by the specimen size, judging from the fact that they were no smaller than in the  $\frac{1}{8}$  in. thick  $\times \frac{3}{4}$  in. diam specimen.

2—The nickel content did not indicate any correlation with the burst temperature as shown by the data of Table IIIa. These results were obtained with a new set of specimens subjected to the same procedure as for the specimens corresponding to Table II.

#### Relation of $M_b$ to $M_s$

Two properties were measured in an attempt to determine whether any transformation took place above  $M_b$ : 1—intensity of magnetization, and 2—electrical resistance. The sensitivity of these methods as used were 1 pct martensite and 0.05 pct martensite, respectively, and hence only the electrical resistance results will be presented here.

The electrical resistance specimens were 1/16 in. diam wires of alloy B. Austenitizing was carried out at 1100°C for 30 min in an atmosphere of prepurified nitrogen, followed by oil quenching to room temperature. A Kelvin double bridge was used for determining the electrical resistance, while the specimens were cooling to subatmospheric temperatures.

Measurements of electrical resistance as a function of temperature yielded curves similar to the one shown in Fig. 3. It is to be noted that the points deviate from a straight line in the temperature

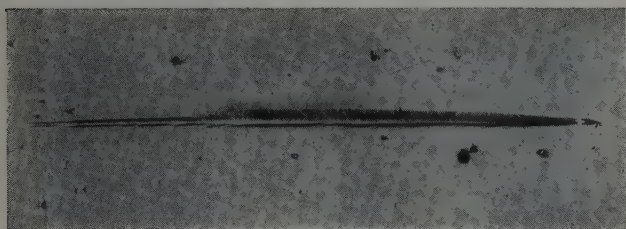


Fig. 4—Upheaval of martensite plate on surface of single crystal of 69 pct Fe-31 pct Ni alloy that had been electropolished prior to subcooling. Note slip in austenite around plate. Oblique illumination. X1500.

range just above  $M_b$ . This result provided the first definite clue that some martensite formation may take place above  $M_b$ .

It seemed worthwhile at this point to determine whether the deviation of the line above  $M_b$  represented a reversible or irreversible process. Accordingly, an electrical resistance vs. temperature curve was run on a specimen to 5° below the temperature at which the curve became nonlinear, but still above the burst temperature. There the cooling was

Table III. Effect of Nickel Content and Plastic Deformation on Burst Temperature of 69 Fe-31 Ni Single Crystals

| a—Austenitized at 600°C             |                                         |            |
|-------------------------------------|-----------------------------------------|------------|
| Ni, Pct                             | Position in $\frac{1}{8}$ In. Diam Disk | $M_b$ , °C |
| 30.98                               | Center                                  | -60        |
| 30.99                               | Periphery                               | -65.5      |
| 31.02                               | Periphery                               | -74.5      |
| 31.09                               | Periphery                               | -60.8      |
| 31.22                               | Midway                                  | -50        |
| 31.38                               | Periphery                               | -59.5      |
| 31.39                               | Periphery                               | -64        |
| 31.43                               | Periphery                               | -70        |
| 31.43                               | Periphery                               | -60.8      |
| b—Plastically Compressed Above 60°C |                                         |            |
| Ni, Pct                             | Degree of Deformation, Pct              | $M_b$ , °C |
| 30.74                               | 10                                      | -48        |
| 31.02                               | 20                                      | -46        |
| 31.09                               | 50                                      | -44.5      |
| 31.12                               | 50                                      | -45        |
| 31.18                               | 50                                      | -44        |

stopped, the specimen was reheated, and resistance measured as a function of temperature. The heating curve did not retrace the nonlinear curve, but remained quite parallel to and below the linear part of the cooling curve. Thus, the deviation from linearity was not reversible. In fact, subsequent metallographic observations demonstrated conclusively that some martensite actually formed above  $M_b$ . The extent of such transformation was estimated by means of a set of curves of electrical resistance vs. percentage of martensite (each curve corresponding to a given temperature) where lineal analysis was employed for calibration purposes. Using these master curves with linear extrapolation to 0 pct martensite, it was found that the maximum amount of martensite formed above  $M_b$  was approximately 0.5 pct in the alloys under consideration. Repetition of these experiments using precision-length techniques yielded the same results.

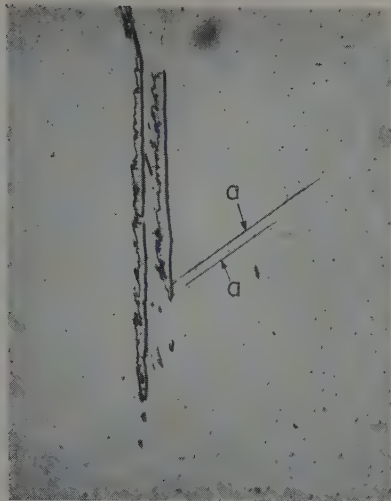
The best metallographic procedure for disclosing the martensite formed above  $M_b$  was to electropolish the austenitic specimen prior to the subcooling and to search meticulously for the upheavals of martensite on the unetched surface after the subcooling. An example of such a martensitic upheaval is given in Fig. 4.

With these results, it was clearly demonstrated that  $M_s$  is higher than  $M_b$  for the specific cases investigated. It is conceivable, however, that  $M_s$  may equal  $M_b$  under different experimental conditions.

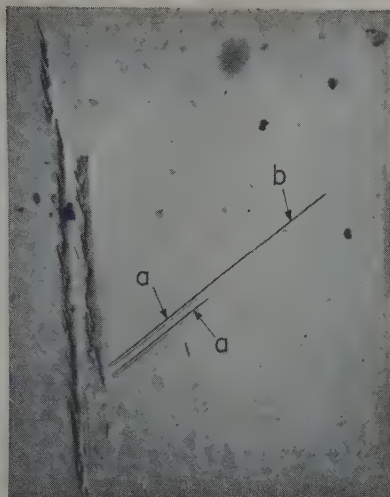
#### Visual Study of Martensitic Plates

The martensite formed above  $M_b$  appears primarily at the surface of single austenite crystals and at the grain boundaries of polycrystals. In the former case, the martensitic plates exist entirely within the austenite crystal (except where they meet the air surface) and do not require grain boundaries or

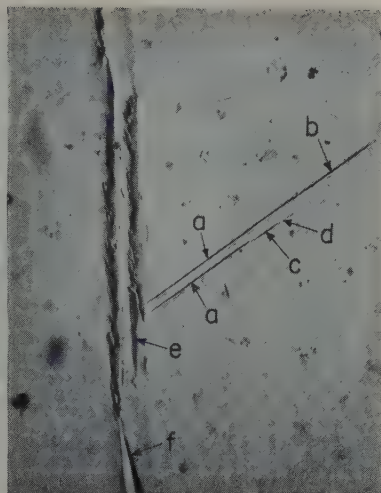




a—Plates *a* formed after electropolishing surface, etching with Marble's reagent and re-quenching to  $-50^{\circ}\text{C}$ . Surface then electropolished and electroetched prior to taking micrograph.



b—Plate *b* formed after re-quenching to  $-50.5^{\circ}\text{C}$ . Surface then electropolished and electroetched.



c—Plate *c* formed after re-quenching to  $-51^{\circ}\text{C}$ . Surface then electropolished and electroetched. On re-quenching to  $-51.5^{\circ}\text{C}$ , plates *d*, *e*, and *f* were formed. Micrographs were then taken without any further surface preparation.

Fig. 5—Martensite plates formed above  $M_b$  at surface of single crystal. Vertical plates formed on initial quench to  $-52^{\circ}\text{C}$ . Oblique illumination. X750.

other plates to inhibit their growth. For example, the plate of Fig. 4 was examined not only on the surface shown but after repeated electropolishing and etching to reveal the complete three-dimensional surroundings. The plate extended below the surface for a distance roughly equivalent to its length in the plane of the surface, and there were no grain boundaries or nearby martensitic plates to prevent further growth. In addition, it was observed that subboundaries (veining) and slip lines in the single crystals did not act as noticeable barriers to the growth of martensitic plates. Fig. 4 provides an illustration of a plate that propagated through a veining boundary. These findings are contrary to the postulation that the plates should grow out to boundaries at which resisting stresses can develop.<sup>8</sup>

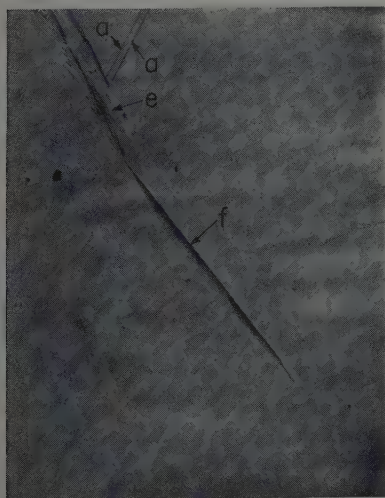
It was noted in these metallographic studies that the ends of the martensitic plates acted as favored (but not exclusive) nucleation sites for the formation of plates which came into being on further cooling (still above  $M_b$ ). Sequences of this phenomenon

are shown in Figs. 5 and 6. The vertical plates of martensite in Fig. 5a were formed at the surface of a single crystal of austenite during a quench to  $-52^{\circ} \pm 0.5^{\circ}\text{C}$ . This surface was then electropolished at room temperature and lightly etched with Marble's reagent\*\*\* to disclose the etched pattern of the plates. The specimen was then quenched to  $-50^{\circ}\text{C}$ ,  $2^{\circ}\text{C}$  higher than previously,<sup>†</sup> and the thin plates marked "a" appeared. The micrograph in Fig. 5a was taken at this stage.

As a next step, the same specimen was quenched to  $-50.5^{\circ}\text{C}$ , and the plate marked *b* appeared. This is shown in Fig. 5b which was taken after re-electropolishing and electroetching at room temperature. Despite the fact that plate *b* seems to be an extension

\*\*\* Copper sulphate 20 g, concentrated hydrochloric acid 100 ml, water 100 ml, ethyl alcohol 200 ml yields a modified Marble's reagent which is very sensitive to the presence of martensite in this alloy.

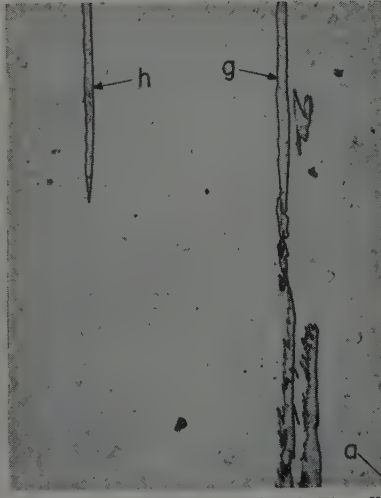
† The martensitic transformation in single crystals is quite sensitive to the state of the surface, which accounts for the increment of transformation during the second cooling.



a—Same as Fig. 5c. Micrograph taken at X375 in order to include all of plate *f*.



b—Same as Fig. 5c. Plates *g* and *h* were formed at same time as plates *d*, *e*, and *f*. Micrograph taken at top of original vertical plate. Compare with Fig. 5b. X750.



c—After taking micrograph of Fig. 6b, specimen was lightly etched with Marble's reagent to bring out transformation. Note that lines at sides of plates *g* and *h* have disappeared indicating they are slip lines. X750.

Fig. 6—Martensite plates formed above  $M_b$  at surface of single crystal. Note that, as in Fig. 5, new plates have appeared at ends of existing plates. Oblique illumination.



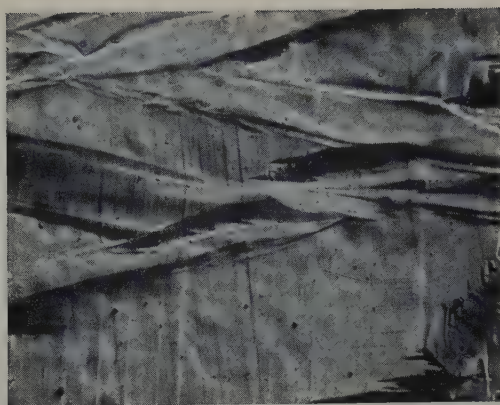


Fig. 7—Micrograph of a previously electropolished surface after a burst of transformation has occurred. Lines shown in micrograph are slip lines. Bending of slip lines indicates that slip occurred prior to the transformation in such regions. X500.

of plate *a*, there is actually a discontinuity between the two, and *b* must be regarded as a new plate that was nucleated at the end of the existing plate.

The micrograph in Fig. 5c was taken on the same specimen after quenching to  $-51^{\circ}\text{C}$ , electropolishing, electroetching, and requeenching to  $-51.5^{\circ}\text{C}$ , with no further surface treatment. Plate *c*, which is etched in Fig. 5c but not present at all in Fig. 5b, formed during the quench to  $-51^{\circ}\text{C}$ . Plates *d*, *e*, and *f* of Fig. 5c, plates *e* and *f* of Fig. 6a and plates *g* and *h* of Fig. 6b are visible as upheavals, and hence must have formed during the last quench to  $-51.5^{\circ}\text{C}$ . The discontinuous nature of the propagation of successive plates is evident. It is also clear that the later plates may or may not have the same orientation as the existing plates, and that the ends of prior-formed plates are activated regions for the nucleation of new plates. (The different orientations merely represent various permutations of the habit  $\pm \{259\}$ ). These findings are in accord with the previous observation that the burst phenomenon is an autocatalytic reaction.

Examination of Figs. 4 and 6b reveals the presence of fine lines in the austenite around the martensitic plates. In order to determine whether these lines were due to slip or to upheavals of tiny martensitic platelets, the specimen of Fig. 6b was lightly etched with Marble's reagent. The resulting structure, shown in Fig. 6c, indicated no trace of the fine lines, and therefore the latter could not have been caused by martensitic platelets. It may be concluded that the lines were slip lines due to plastic deformation of the austenite. This supports the suggestion of Kurdjumow<sup>7</sup> that plastic flow around the martensite produces a loss of coherency and limits the size of the plates. By the same token, the plate thickness is not controlled by a balance between the driving free energy and elastic restraining energy, and calculations<sup>8</sup> based on such an hypothesis can have little significance, at least for Fe-base alloys in which large transformation strains occur.

Additional evidence contrary to the energy-balance hypothesis was obtained from a study of martensitic plate-thickness vs. temperature in the martensite range, which demonstrated that existing plates do not increase in thickness during cooling. According to the above hypothesis,<sup>8</sup> the plates should thicken by 33 to 700 pct (depending on the extremes

in thermodynamic data found in the literature<sup>9, 10</sup>) on cooling between  $-20^{\circ}$  and  $-90^{\circ}\text{C}$ , but no such change was found. In a few instances, the apparent thickness increased due to the formation of platelets alongside the original plate, but this took place stepwise with decreasing temperature.

The specimen of Figs. 5 and 6 was finally cooled to  $-64^{\circ}\text{C}$  where the burst occurred. A typical region of the resulting upheavals is given in Fig. 7. Clearly, the average thickness of plates formed in the burst is many times larger than that of plates formed above  $M_b$ . This signifies that during the burst the stresses developed at the side-boundaries of the transforming plates are much less for a given plate thickness (and therefore the plates can grow much thicker before plastic flow occurs) than in the case of plates forming above  $M_b$ . The foregoing conclusion seems reasonable in the light of the fact that there are at least four different permutations of the  $\pm \{259\}$  habit<sup>†</sup> which tend to move the adjacent austenite in about the same direction when martensite forms cooperatively along these planes.<sup>1</sup>

Fig. 7 also shows numerous slip lines which are bent where they cross martensite plates. This indicates that extensive slip may take place during the burst in some regions prior to the formation of martensite there. Moreover, it means that such slip lines are not sufficiently strong barriers to prevent the propagation of martensite.

Two important questions are raised by the above results: 1—What is the criterion for the triggering of the burst? 2—What is the significance of the fact that the ends of existing plates are favored nucleation sites for new plates?

A tentative answer to the first question is obtained from consideration of some additional experiments. It has been found that room temperature alteration of the state of the surface of a single crystal after quenching to a given subatmospheric temperature may induce a burst on requeenching to that same temperature. Furthermore, it has been noticed that bursts may occur isothermally in polycrystalline specimens after some time at a subzero temperature (held constant within  $\pm 0.2^{\circ}\text{C}$ ), either with or without a measurable change in resistivity occurring prior to the burst at that temperature. It has also been observed that rapid quenching of 1/16 in. diam polycrystalline wires into a bath at  $-77^{\circ}\text{C}$  can depress  $M_b$  by about  $20^{\circ}\text{C}$  as compared to slow cooling. These findings indicate that the triggering of the burst does not take place at a characteristic temperature for the alloy at hand, but is sensitive to other experimental variables.

In the light of ref. 1, a possible criterion for the onset of the burst is that a number of plates, which have the same direction of adjacent austenite motion and which bound the same region of austenite, must be nucleated almost simultaneously. Under these conditions, it appears that stresses are transferred to other austenite regions where new plates can be activated. Undoubtedly, the momentum of the process helps to increase these stresses. The activation can occur either at existing regions of strain or even in previously strain-free regions, if sufficient stress of the proper direction is developed.

This mechanism for producing the burst leads to the observed structure-sensitivity of the burst tem-

<sup>†</sup> In systems having the  $\pm \{225\}$  habit, the degree of cooperation as measured by the number of austenite directions of motion within the same solid angle used for the  $\pm \{259\}$  case, is roughly about one half that for the latter.



perature because the probability of activating an embryo is affected by the prior state of internal strain at the embryo. The mechanism also provides for autocatalytic action through the dynamic as well as static stresses developed by the cooperative displacements. Consequently, it can be predicted that bursts will not occur as markedly in other systems where the crystallography of the transformation happens to permit less cooperation than in these alloys. For example, the cooperative effect is not so great for systems with  $\{225\}$ † habits as for systems with  $\{259\}$  habits. Thus, it may be expected that the burst phenomenon will not be so prominent in ordinary steels as in these Fe-Ni alloys.

Let us now consider the significance of the preferential nucleation of martensite above  $M_s$  at the ends of isolated martensite plates. It is very likely that the magnitude of the internal stress in the austenite bounding an isolated martensite plate is largest at the rim of the plate. The consequence of this situation can be interpreted in at least two ways. According to the theory of martensite nucleation via athermal<sup>8</sup> embryos of the martensitic phase, stress should act to decrease the critical size of the embryos, and hence stressed regions should be favored sites for nucleation. However, inasmuch as the volume of the highly stressed region about the rim of an isolated martensite plate is extremely small, either the critical size would have to be an exceptionally sensitive function of stress, or the concentration of athermal embryos would have to be very high. An alternate interpretation, according to the theory of martensite nucleation via strain embryos,<sup>2</sup> is that the region of internal stress at the rim becomes an embryonic region of large strain and appropriate direction of strain to nucleate additional martensite. Although there does not appear to be any way of positively distinguishing between these theories from the data obtained so far, an important conclusion can be drawn; that is, whether the new martensite is nucleated at existing martensite rims by athermal embryos or not, the nucleation there is controlled by the internal strains and not by the distribution of athermal embryos. Inasmuch as any real specimen contains many internal strains, this conclusion might be generalized to include internal strains other than those at the martensite plates. It is important to note here that the plates appearing above  $M_s$  are not nucleated exclusively by the prior-formed martensite. This applies to the plate in Fig. 4 and, of course, to the original plates in Fig. 5.

Further experimental verification of the above deduction as applied to the general transformation is given in the next section.

### Athermal Nucleation

The aspect of the athermal nucleation theory that was checked was the supposed role of an equilibrium statistical-mechanical distribution of martensitic embryos at the austenitizing temperature. According to this concept, the amount of martensite produced for a given temperature in the martensitic range, and for a given grain size, is a function of the martensitic embryo distribution, and hence of the austenitizing temperature. Thus, one series of specimens was subjected to the cycle illustrated in Fig. 8a, another to the cycle of Fig. 8b, and a third to the cycle of Fig. 8c. In all instances, the heating

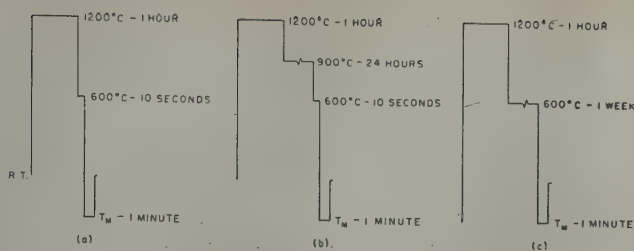


Fig. 8—Temperature-time cycle to determine effect of austenitizing temperature on martensite range curve.

for 1 hr at 1200°C “set” the grain size which did not change during the subsequent treatments. In case b, the temperature was then lowered to 900° for 24 hr to establish an embryo distribution characteristic of this temperature. In case c, the holding time at 600°C was for one week. In cases a and b, the quench to room temperature was interrupted momentarily at 600°C so that the final quenching stresses would be the same in the three series, after which the subzero transformation was determined immediately. Direct quenching was also conducted from 1200° and 900°C to room temperature, but there was no effect on the results and hence the interruption at 600°C was actually not a factor.

The results obtained from these experiments, given in Fig. 9, show that the amount of transformed phase is independent of the austenitizing temperature, grain size being maintained constant. It may therefore be concluded that athermal embryos of the martensitic phase, if they exist at all, do not activate the martensitic transformation in these Fe-Ni alloys. It may further be inferred, from the generality of the concept, that this negative conclusion also applies to other materials.

### Experiments Relating to Strain Embryos

Having demonstrated that the possible existence of statistical distributions of martensitic embryos in the austenitic phase was irrelevant to the problem under consideration, it appeared worthwhile to investigate the alternate suggestion that the embryos for the martensitic reaction are comprised of regions of internal strain in the austenite<sup>2</sup> (e.g., accidental lattice disturbances or dislocations). On this basis, it would be predicted that a cold-worked sample should undergo transformation at a higher temperature than a non-cold-worked sample. Moreover, specimens as cut from a single-crystal ingot should transform at higher temperatures than similar specimens after stress relieving. Because plastic deformation of polycrystals may introduce barriers to the transformation as well as the higher energy strain embryos being sought, it was decided to per-

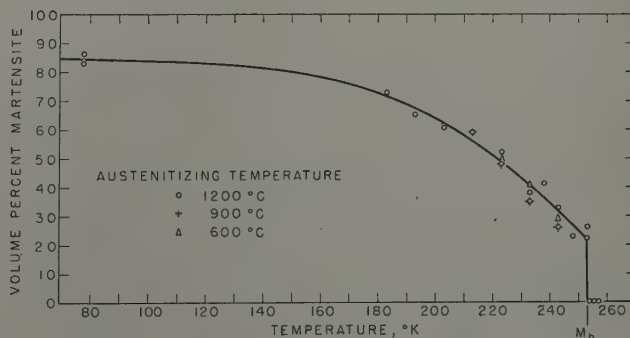


Fig. 9—Martensite range curve for 70.5 pct Fe-29.5 pct Ni alloy. Austenitizing temperature varied according to cycles in Fig. 8.

† The exact agreement of some of the data in Fig. 9 is considered fortuitous.

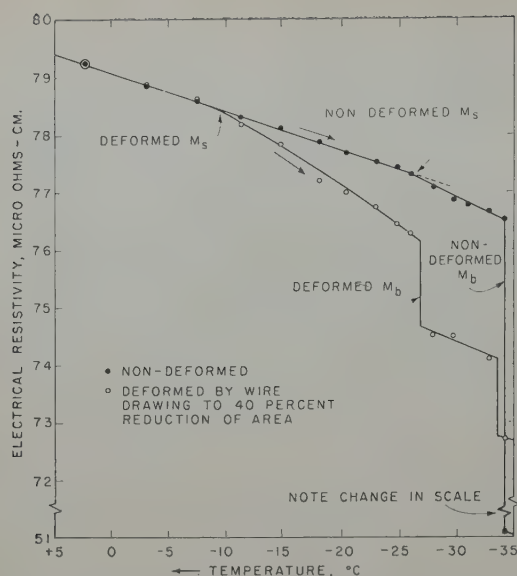


Fig. 10—Effect of plastic deformation performed above  $M_d$  ( $60^\circ\text{C}$ ) upon subsequent martensite transformation in 70.5 pct Fe-29.5 pct Ni alloy.

form these experiments first with single crystals of alloy A.

Several cube specimens,  $\frac{1}{4}$  in. on a side, were cut from a single crystal of austenite, then stress relieved at  $600^\circ\text{C}$ , and refrigerated to ascertain the  $M_b$  temperatures. Similar stress-relieved specimens were compressed by 10 to 50 pct at a temperature above  $M_d$  ( $\sim 60^\circ\text{C}$ ), and the  $M_b$  temperatures were determined. Two single-crystal ingots were used. The results with specimens from one ingot (Table III) showed that the average  $M_b$  temperature was raised from  $-63^\circ$  to  $-46^\circ\text{C}$  by the cold working, and that the inherent spread in these values was markedly reduced. For specimens from the second ingot, the average  $M_b$  temperature was raised from  $-55^\circ$  to  $-47^\circ\text{C}$  by cold working.

Further verification was obtained in the following way: A  $\frac{1}{8}$  in. cube single crystal was cooled to as low a temperature as possible, called the reference temperature, above  $M_b$ . Then the specimen was heated above the  $M_d$  temperature, compressed 10 pct and cooled back to the reference temperature. If no burst occurred during this cooling, the specimen was heated back above  $M_d$ , compressed further, and the cycle repeated to determine whether a burst would ultimately occur on cooling to the reference temperature. The results definitely proved that plastic deformation above  $M_d$  raises the burst temperature. For example, compression in the range of 10 to 35 pct raised  $M_b$   $4.5^\circ$  to  $7.5^\circ\text{C}$  above the reference temperature from its previous level below the reference temperature.

Another manifestation of this phenomenon was shown by comparison of the  $M_b$  values for specimens as cut from the single-crystal ingot with those for similar specimens after stress relieving at  $600^\circ\text{C}$ . The average  $M_b$  of the annealed crystals was  $15^\circ\text{C}$  lower than the average  $M_b$  of the as-cut crystals. The strain-embryo concept is consistent with all these experiments on single crystals.

Previous investigators<sup>11, 12</sup> have reported that plastic deformation of polycrystalline alloys usually has a stabilizing effect on the subsequent transfor-

mation. This trend is contrary to the results just described for single crystals. In order to ascertain the reason for the anomaly, experiments were performed with polycrystalline wires of alloy B in the following way. Several wires,  $\frac{1}{16}$  in. diam, were first austenitized in an evacuated Vycor tube at  $1100^\circ\text{C}$  for 30 min, then quenched in water to room temperature. Reductions in area of 0, 10, 20, 30, and 40 pct were achieved by drawing the wires through dies while kept above  $M_d$  ( $\sim 60^\circ\text{C}$ ). Immediately after this plastic deformation, each specimen was subcooled, and the electrical resistance measured as a function of the temperature.

The results of these experiments can be summarized as follows: With increasing amounts of plastic deformation (up to 40 pct reduction in area) above  $M_d$ : 1— $M_s$  was raised progressively (40 pct reduction in area corresponded to an increase in  $M_s$  of about  $17^\circ\text{C}$ ). 2— $M_b$  was first increased slightly, then decreased. 3—At temperatures somewhat below  $M_b$  of the nondeformed specimen, the amount of transformation was less, the greater the amount of deformation. These characteristics are illustrated in Fig. 10, which shows the temperature-resistivity curves for specimens having 0 and 40 pct reduction in area subsequent to austenitizing.

The above relationships clearly indicate that there are two opposing effects of prior plastic deformation on the martensite transformation during subsequent cooling. The first effect is an increase in the magnitude of the submicroscopic internal strains, and thus martensite can be nucleated at higher temperatures. This accounts for the fact that  $M_s$  increases with the extent of plastic deformation. The second effect of plastic deformation, appearing primarily in polycrystalline alloys, is to "subdivide" the grains into smaller units as a result of the inhomogeneous nature of the deformation (the formation of kink bands and deformation bands provides an effectively finer grain size). Because the average length of plate formed from a given strain embryo is smaller in the "subdivided" grains, the volume of martensite per activated embryo would be expected to decrease with increasing plastic deformation. Hence, even though there is an increase in the number of embryos activated at any given temperature, the actual amount of transformation may be less. The net result of plastic deformation is a combination of these two opposing effects. A somewhat similar conclusion has been reached by Kurdjumow<sup>13</sup> in his studies on the influence of prior plastic deformation on the subsequent isothermal martensite transformation.

The two opposing trends also bear directly on the  $M_s$  temperature. As  $M_s$  is raised by plastic deformation,  $M_b$  is also raised; but with increasing amounts of deformation as applied to polycrystals, the partitioning of the austenite caused by inhomogeneous deformation makes it progressively more difficult for the burst to occur. Consequently,  $M_b$  then begins to drop. This characteristic may be regarded as a grain-size effect, which is discussed in the next section.

### Constraint and Grain Size Effects

The explanation of the burst phenomenon herein presented predicts that if restraint is provided at the boundaries of the single crystal then the burst temperature should be depressed, but not necessarily the  $M_s$  temperature. To test this prediction the following experiments were performed: Single crystals of alloy A,  $\frac{1}{16} \times \frac{1}{8} \times \frac{1}{8}$  in., which had been serrated on their faces to provide a good mechanical bonding

<sup>††</sup>  $M_d$  is the temperature above which austenite is not converted into martensite by plastic deformation.<sup>11</sup>



surface and etched for 1 hr to remove the cold-worked surface layer, were stress relieved at 600°C and mounted in bakelite with a 1/16x1/8 in. polished face exposed. Control specimens from adjacent positions in the single-crystal ingot were also mounted in bakelite in exactly the same manner, then removed carefully from the bakelite by cutting the bakelite away from the sides with a jeweler's saw. The  $M_s$  temperatures of the control specimens were determined by immersing in cold baths at lower and lower temperatures until the burst took place. This was detected audibly by the "click" as well as by the visible evolution of bubbles in the bath due to the heat of transformation. Also after heating back to room temperature, the martensite could be seen by microscopic examination on the polished surface.

Before the burst temperatures of the bakelite-constrained specimens were determined, a run was conducted to establish the time required for the specimen to reach within 1° of the bath temperature. It was found that about 3 min were required. Accordingly, the bakelite-constrained specimens were kept in the bath for 6 min in order to insure that the bath temperature was reached. Exactly the same methods were used for observing the burst in the bakelite-constrained specimens as in the case of the control specimens. The results obtained are given in Table IV.

It is evident that the bakelite-constraint caused a lowering of the burst temperature. The extent of depression of  $M_b$  ranged from about 15° to 20°C. (The good reproducibility of burst temperatures for the control specimens was undoubtedly due to the fact that the mounting in bakelite introduced some strain into the specimens.)

According to the ideas presented here to account for the burst phenomenon, there should be small amounts of martensite in the constrained specimens at a temperature above their  $M_b$  and below the  $M_s$  of the control specimens. When painstaking care was taken in preparing and examining the surfaces of the specimens, such small amounts of transformation were detected.

A further prediction stemming from this picture of burst formation is that, if two different sizes of specimens are constrained, the smaller specimens should burst at the lower temperature. This follows from the fact that with a given surface constraint, more resistance to the burst transformation is generated in the smaller specimen than in the larger one, other things being equal. To test this consequence, two sizes of single crystals were mounted in bakelite. One was 1/4x1/4x1/4 in. and the other 1/32x1/8x1/8 in. The average  $M_b$  values so obtained were: -38.5°C (free control specimen), -50.5°C (large constrained specimen), and -55°C (small constrained specimen).<sup>‡‡</sup>

Constraint may also be achieved if the crystal is surrounded by other crystals in the form of a polycrystalline aggregate. In order for the chain of transformation to continue, the austenite along the

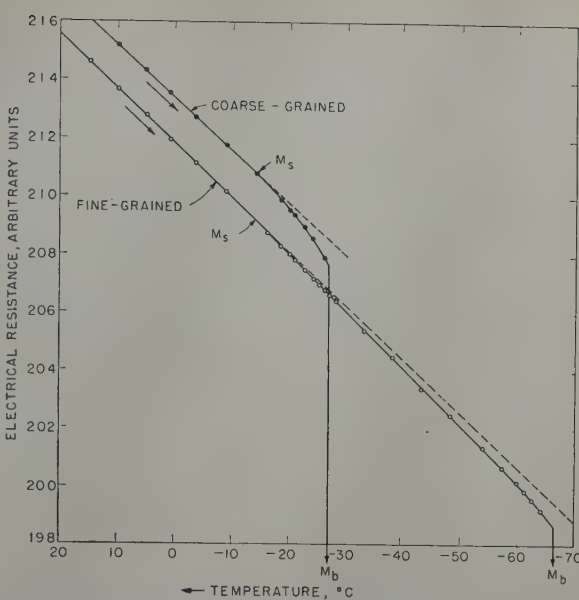


Fig. 11—Electrical resistance vs. temperature curves for specimens having A.S.T.M. No. 4-5 and A.S.T.M. No. 9 grain size. Alloy of 70.5 pct Fe-29.5 pct Ni.

side of the transforming plate must be able to move. If it is constrained by a rigid material such as bakelite, then a chain of transformation, once started, would be quickly stopped by the resistance to motion developed at the boundaries, and the temperature would have to be decreased to overcome this resistance. In a similar way, grains of different orientation at the boundaries of the crystal can act as constraints, from which it follows that the burst temperature should decrease with decreasing grain size, even though the  $M_s$  temperature may not be appreciably affected.

To check the predicted effect of grain size, electrical resistance measurements were made on 1/16 in. diam wires of alloy B having grain sizes of ASTM No. 9 and ASTM No. 4-5. The first series of specimens was austenitized at 760°C for 20 min and the second series was austenitized at 1100°C for 1 hr. All of the specimens were oil quenched to room temperature. The results of these measurements are given in Fig. 11.

Two points are immediately clear. One is that the  $M_b$  of the fine-grained material is about 40°C lower than that of the coarse-grained material. The other is that the deviation from linearity in the resistance vs. temperature curves starts at about the same temperature in both cases. Subsequent metallographic investigation showed that the deviation from linearity is associated with the formation of martensite plates above  $M_b$ .

This phenomenon was checked in still another way. Length measurements made during subcooling and reheating in a high precision linear coefficient of expansion apparatus<sup>14</sup> agreed unambiguously with the electrical resistance determinations in disclosing the existence of transformation above  $M_b$  in both the coarse-grained and fine-grained material. Thus, the predictions of grain size upon both  $M_b$  and the transformation above  $M_b$  were confirmed. According to these results,  $M_s$  is not sensitive to grain size, if it is defined as the temperature at which the martensitic reaction starts.

To account for the grain-size effect on  $M_b$  on the basis of the nucleation and growth theory,<sup>8</sup> it is

<sup>‡‡</sup> These three  $M_b$  values happen to be higher than those given in the previous tables because of an unusually low Ni content.

Table IV.  $M_b$  Values for Constrained vs. Free Specimens

| $M_b$ , °C   |             |                |
|--------------|-------------|----------------|
| Free Control | Constrained | Difference, °C |
| -51.5        | -67.5       | 16             |
| -50          | -70         | 20             |
| -51          | -70         | 19             |
| -51          | -72         | 21             |

necessary to assume that, with decreasing grain size, the plates become thinner in proportion to their decreasing length, and hence become more difficult to detect under the microscope. However, no such dependence of thickness on length was found. Within a very wide range of grain sizes,§§ the plates formed at  $M_b$  were comparatively constant in width, despite enormous differences in length.

It was observed that the amount of transformation involved in the burst often decreased with decreasing grain size and that the transformation sometimes occurred isothermally over a measurable period of time. This phenomenon will be discussed in another paper.

### Summary and Conclusions

The first substantial ( $> \frac{1}{2}$  pct) amount of transformation in 70 pct Fe-30 pct Ni alloys occurs within the interval of an audible click at a temperature called  $M_b$ . This phenomenon, designated as a burst, was investigated experimentally using both single and polycrystalline specimens with the following results:

1—The reaction occurring during the burst is autocatalytic, that is, the first transformation to appear in the burst provides the impetus for the nucleation of succeeding plates and so on.

2—Martensite forms in amounts up to  $\frac{1}{2}$  pct above  $M_b$ , ( $M_b$  is lower than or equal to  $M_s$ ) and new plates are nucleated preferentially at the rims of previously formed plates on decreasing the temperature.

3—Plastic deformation (slip) takes place locally at the martensite-austenite interface in plates formed above  $M_b$ , while substantial amounts of widely dispersed slip occur in the austenite during the burst.

4—The thickness of plates formed above  $M_b$  is very much less than that of plates formed during the burst.

5—Constraint to change-of-shape as offered by bakelite depresses  $M_b$  but not  $M_s$ , and a decrease in the size of the specimen being constrained enhances the depression of  $M_b$ .

6—Decrease in grain size depresses  $M_b$ , but does not measurably affect  $M_s$ .

7—Prior plastic deformation in single crystals raises  $M_s$  and  $M_b$ , and reduces markedly the range of scatter of  $M_b$  values. Prior plastic deformation in polycrystals raises  $M_s$ , first raises then lowers  $M_b$ , and decreases total amount of transformation measured below the  $M_b$  for zero deformation.

Additional experiments were conducted to check the validity of the nucleation and growth theory as applied to the burst phenomenon, with the following results:

1—Once formed, the martensitic plates do not thicken with decreasing temperature, as required by this theory.

2—The martensite range curve below  $M_b$  is insensitive to the austenitizing temperature for the Fe-Ni alloys, which demonstrates the independence of the transformation upon distributions of athermal martensite embryos.

3—The grain size explanation based on nucleation and growth is invalid for two reasons: (a) Plates can exist which are not bounded at the ends by existing plates, grain boundaries or other such obstructions. (b) A direct dependence of plate thick-

ness to length is predicted by the theory, and is not found when the grain size is decreased.

4—The concept of loss of coherency due to plastic flow in limiting the size of plates, as proposed by Kurdjumow, has been found to be consistent with experiment.

It is concluded that regions of internal strain are preferential sites for nucleation of martensite in these alloys. Two such regions are the internal strains within the virgin austenite and the internal strains at existing martensite plates. It appears that the nucleation is more sensitive to the state of strain than to variations in composition.

A tentative explanation for the burst phenomenon has been presented. Use is made of the cooperative nature of the reaction in these alloys to nucleate new plates and thus generate a chain of transformation.

The possibility exists that many martensitic transformations involve bursts, to a greater or lesser extent. If this proves to be the case, the burst phenomenon may provide a new basis for understanding important features of the martensitic transformation.

### Acknowledgments

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# Fundamental Effects of Cold Working on the Creep Resistance of an Austenitic Alloy

by D. N. Frey and J. W. Freeman

**Fundamental reasons for the improvement in creep resistance of an austenitic alloy by cold working were investigated mainly by X-ray diffraction. The creep resistance was found to be improved by the internal stresses in the lattice of the alloy induced by the cold work.**

**T**HIS investigation was concerned with the fundamental reasons for improvement in creep resistance of an austenitic alloy as a result of cold working. Also, the investigation was carried out to elucidate the conditions under which cold working could be expected to improve the creep resistance.

To achieve these ends, creep resistance and internal structure were correlated for a variety of cold-worked conditions. Since the aim of the investigation was not to obtain specific and extensive information on any one alloy, creep testing was done with a single stress at 1200°F. Structural studies were carried out primarily with X-ray diffraction characteristics. The alloy used, low carbon N-155, was selected on the basis of being representative of at least some of the alloys used in gas turbines.

Low carbon N-155 alloy in the form of 7/8-in. sq bar stock was used in this investigation. The chemical composition, in percent, was: C, 0.13; Mn, 1.43; Si, 0.34; Cr, 20.73; Ni, 18.92; Co, 19.65; Mo, 3.05; W, 1.98; Cb, 0.98; N, 0.14; and Fe, balance.

The bar stock was produced from a 13-in. sq billet, finished to 7/8 in. round cornered square between 2060° and 1910°F.

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Prior to use in this particular investigation, the bar stock was solution-treated 1 hr at 2200°F and water quenched. This procedure was used in order to put the stock in a condition where effects of prior processing were minimized.

## Experimental Procedure

The specific approach to the problem was two-fold. First, the influence of cold working, under various conditions, on the creep rate under a single stress at 1200°F and on the internal structure was in part determined. Second, the effect of annealing at various times and temperatures on the creep rate and internal structure of the cold-worked samples was in part evaluated. The first step was basic to the investigation—creep resistance and structure were to be correlated. The second step was taken to see if the annealed samples showed some internal changes which could also be correlated with changes in creep resistance. This it was felt would facilitate solution of the basic problem.

The creep and structural studies were carried out on samples reduced approximately 5, 15, and 40 pct at room temperature and 15 pct at temperatures up to 2200°F. Annealing of various of the samples was done at 1200°, 1400°, 1600°, and 1800°F for time periods up to 1000 hr. Studies of the annealed samples were concentrated on materials rolled approximately 5, 15, and 40 pct at room temperature and 15 pct at 1400°F. The creep tests were carried out at 1200°F under 40,000 psi, the latter being approximately the 1000 hr rupture stress of the material

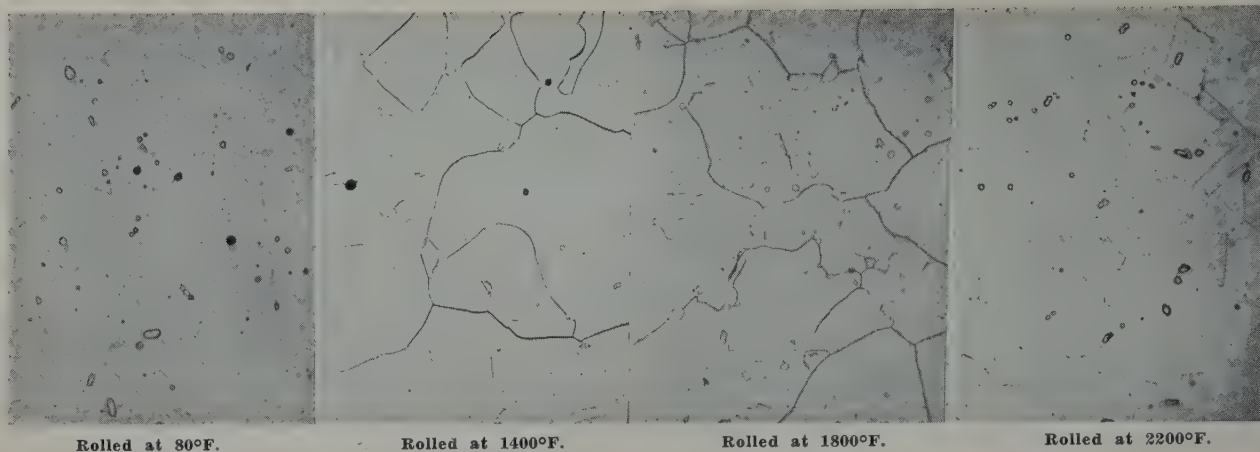


Fig. 1—Effect of rolling temperature upon microstructure of solution-treated low carbon N-155 alloy reduced 15 pct. Electrolytic chromic acid etch. X1000. Area reduced approximately 70 pct for reproduction.

cold reduced 15 pct. No transient creep was observed, and all tests were run for time periods of from 200 to 500 hr, which was sufficient time to establish the steady state creep rate. All creep data are reported in terms of this steady state rate. The estimated accuracy of these rates was  $\pm 40$  pct.

The structural effects of cold working were studied primarily by X-ray diffraction, although microscopic examination, both optical and electronic, was also used. For the diffraction work, surfaces normal to the bar axis were prepared by electrolytic removal of a minimum of 0.020 in. of metal. This was done to avoid artificially cold-worked metal produced by the sample preparation process itself. Conventional metallographic methods were employed, including the use of uranium shadow-cast Formvar replicas in the electron microscope.

Previous work has shown that broadening of diffraction lines occurs as a result of cold working.<sup>1</sup> This has been ascribed both to particle size broadening from fragmentation of the grains and to a distribution of lattice parameters resulting from residual elastic stresses. It was felt that either effect would be important as far as creep resistance was concerned, and accordingly the width of the (220) line of the austenite was photographically recorded as a function of the various rolling and heat treatments. Chromium radiation was used to eliminate fluorescent effects, and with this radiation the (220) line was at  $67^\circ \theta$ , where fair resolution was obtained. The specimen was mounted normal to the X-ray beam and rotated slowly about an axis parallel to, but offset from the X-ray beam. This latter was occasioned by the desire to cover the largest possible

area on the sample surface (cover more grains), and thus obtain diffraction lines with uniform blackening along the diffraction cone.

The width of the (220) line was then taken at a density half way between that of the top and bottom of the line. Correction for instrumental broadening was done by the method of Warren<sup>2</sup> and by further assuming that the broadness of the (220) line from the solution-treated sample was due entirely to instrumental broadening and using it as the instrumental broadening factor in Warren's formula. All broadening data reported thus are relative to the solution-treated sample. The reproducibility of line widths was not better than  $\pm 10$  pct.

As an aid to determining the basic cause of the line broadening observed, integrated intensity measurements were made on the (111) line of some of the cold-rolled and cold-rolled and annealed samples. Here it was anticipated that extinction\* effects would be of major interest. Inasmuch as the lowest order line shows maximum intensity variation with variation in amount of extinction, the (111) line was used. In particular, it was necessary to determine the variation of (111) line intensity with variation of the angle between the (111) planes contributing to the intensity measurements and the rolling direction in the bar. For this, samples were mounted in a Schultz fixture<sup>3</sup> and placed in the Norelco spectrometer, where intensity measurements were taken at  $5^\circ$  or  $10^\circ$  intervals from  $0^\circ$  to  $90^\circ$  with respect to the rolling direction. To cover this range from  $0^\circ$  to  $90^\circ$ , two sample surfaces were used—one parallel and one normal to the rolling direction. Data were taken from each of these samples over a  $50^\circ$  range. This was necessitated by the fact that Schultz's method breaks down over an angular range of more than about  $50^\circ$ . Over the  $50^\circ$  range used, checks were made with randomly oriented samples to insure the applicability of Schultz's method. A standard of comparison for these intensity measurements was a randomly oriented powder compact made of low carbon N-155 filings prepared so that extinction was believed negligible.

### Structural Alterations as a Result of Cold Working

From a microstructural standpoint little change was observed in samples rolled at room temperature until reductions of the order of 15 pct were reached, at which reduction a very few slip lines or bands

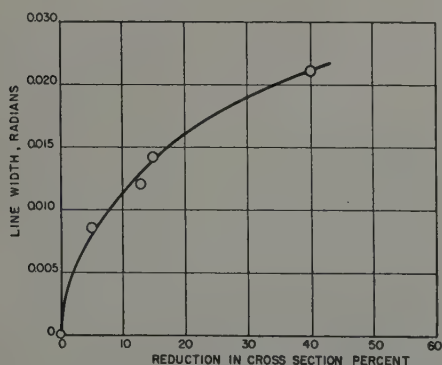


Fig. 2—Effect of reduction at  $80^\circ\text{F}$  on width of (220) line of solution-treated low carbon N-155 alloy.

\* Extinction is the loss of intensity of the diffracted beam due to increasing loss of energy in the primary beam as diffraction itself occurs.



could be observed in polished and rather heavily etched samples. Increasing degree of reduction resulted in greater density of such lines, at least up to reductions of 40 pct.

Increase in the rolling temperature with the degree of reduction held constant at 15 pct resulted in several microstructural changes. From 80° to 1800°F, the grains become more clearly outlined, with possibly some precipitate actually formed at the boundaries at the higher temperatures, see Fig. 1. The change was similar to that obtained when solution-treated material is simply heated at the various rolling temperatures for about 1 hr. After rolling at 2200°F, recrystallization was evident, see Fig. 1. A check on material rolled at 2050°F revealed no recrystallization; it appeared much the same as material rolled at 1800°F. The simultaneous recrystallization temperature† of low carbon N-155 for reductions of 15 pct may thus be placed between 2050° and 2200°F. Greater reductions would probably lower this temperature.

For an interpretation of the widening of the (220) line after rolling, see Fig. 2, reference should again be made to the two possible causes of line broadening due to "cold" work. They are fragmentation of the matrix into crystallites which must have thicknesses less than 1000Å to cause broadening, or the introduction of a range of interplanar spacings, (100) spacings in this case, in turn due to the presence of residual elastic stresses.

In order to separate these two causes of line broadening, use was made of the fact that if the observed broadening were due to crystallites, the crystallites would have to be so small as to preclude any extinction being present. Accordingly the first step in the separation of the two causes of line broadening was to make measurements of the (111) line integrated intensity in order to determine the extinction coefficients‡ of cold-rolled material.

However, before these intensities could be interpreted in terms of extinction coefficients a further complication had to be considered. An intensity increase could be due not only to reduction in extinction, but also to preferred orientation of the crystallites. This latter would act to increase the intensity of various diffraction lines in certain directions relative to the bar axis, such increase not having any relation to a decrease in extinction.

Fig. 3 shows a more detailed study of the intensity of the (111) line at various angles to the rolling direction of materials reduced 15 and 40 pct at 80°F. The curves of Fig. 3 may be taken as representing the relative number of crystallites having the various indicated orientations with respect to the bar (rolling) axis. Further study showed that the preferred orientation was of the "fibred" type with two components (111) and (100). The crystallite distribution about any axis parallel with the bar axis was found to be random. In order to obtain the change in (111) line intensity due to rolling and corrected for the preferred crystallite orientation, use was made of an important feature of Fig. 3. With no change in extinction, the areas of the curves from 0° to 90°, relative to the rolling direction, would re-

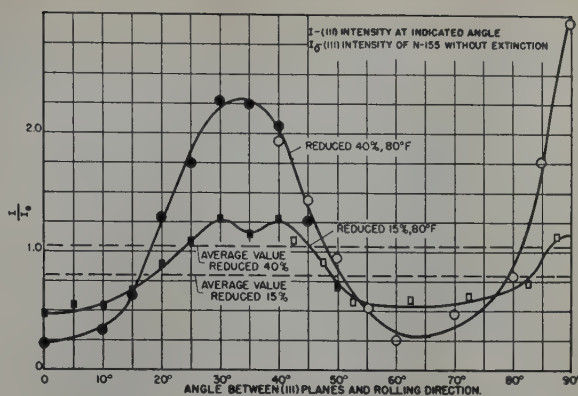


Fig. 3—Effect of rolling at 80°F on (111) intensity at indicated angles with the rolling direction of solution-treated low carbon N-155 alloy.

main constant to a very close degree, irrespective of whether the fibred orientation is present or not. Thus, any change in this area is due to extinction effects. For the particular curves of Fig. 3 the height of a rectangle running from 0° to 90° equalling the above-mentioned area would give the (111) line intensity, relative to the extinctionless low carbon N-155 powder compact, of a material having the same crystallite size as the rolled bars but with the crystallites completely random.

Construction of such rectangles was carried out on Fig. 3. For the material rolled 15 pct at 80°F, the resulting (111) intensity relative to the standard was 0.80 and for the material rolled 40 pct, 1.05. The same figure for the plain solution-treated, low carbon N-155 was 0.77. The estimated accuracy for all of these figures was  $\pm 5$  pct.

Since the standard of comparison for the intensity measurements on Fig. 3 was powdered low carbon N-155 with no extinction, the above figures represent extinction coefficients. It is obvious therefore, that rolling 15 pct hardly reduced extinction in low carbon N-155 over what it was without rolling, while rolling 40 pct eliminated extinction at least to within the experimental error.

If these values at the extinction coefficients are entered into the Darwin formula for extinction as a function of crystallite size, it is found that the as-solution-treated low carbon N-155 and the stock rolled 15 pct had crystallite sizes of the order of  $10^{-4}$  cm, while all that can be said for the stock rolled 40 pct is that its average crystallite size was probably less than  $10^{-5}$  cm.

Going back to the original problem of separating particle size broadening from residual strain broad-

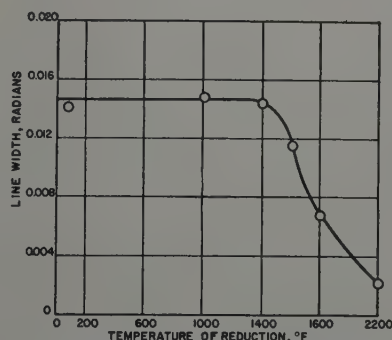


Fig. 4—Effect of rolling temperature on width of (220) line of solution-treated low carbon N-155 alloy reduced 15 pct.

† The simultaneous recrystallization temperature is defined as the temperature of rolling or forging, where recrystallization takes place during or just after working, as evidenced by a finer grain size after cool down than was present prior to working.

‡ The extinction coefficient is here defined as the ratio of the observed (111) integrated intensity to the (111) integrated intensity from a powdered sample of low carbon N-155 believed to have no extinction.

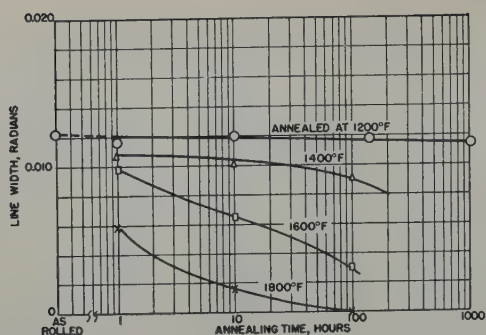


Fig. 5—Effect of annealing on width of (220) line of solution-treated low carbon N-155 alloy reduced 13 pct at 80°F.

ening, the Scherrer formula shows that small particle line broadening is negligible with particles greater than  $10^{-5}$  cm, and so particle broadening was certainly absent in solution-treated low carbon N-155 cold reduced up to 15 pct and of unknown proportions in the material reduced 40 pct. It can thus be concluded that for a cold reduction of 15 pct, the line broadening which occurred was due entirely to residual elastic strains, while the line broadening in samples reduced 40 pct could be due in part to small particle size but not very probably. Accordingly, line widths shown in Figs. 2 and 4 may be considered as indicating some average value of the internal "locked up" stresses present after the various treatments indicated.

Fig. 2 indicates that the internal stresses did not increase uniformly with degree of reduction, but rather that the internal stresses apparently would reach a maximum value independent of further reduction. Such results have been noted before by many investigators.

Fig. 4 shows that rolling 15 pct up to temperatures of approximately 1500°F resulted in the same average internal stress. Increasing the temperature of reduction past this point reduced the internal stresses, and rolling at temperatures of about 2200°F resulted in practically no residual internal stresses. It appears that the amount of relaxation of the internal stresses occurring during or just after the rolling operation (during cool down) is the factor which limits the line widths obtainable at the higher rolling temperatures.

Microstructural examination of all the various annealed samples revealed that only the material reduced 40 pct at 80°F recrystallized. This recrystallization started after about 10 hr at 1600°F and was

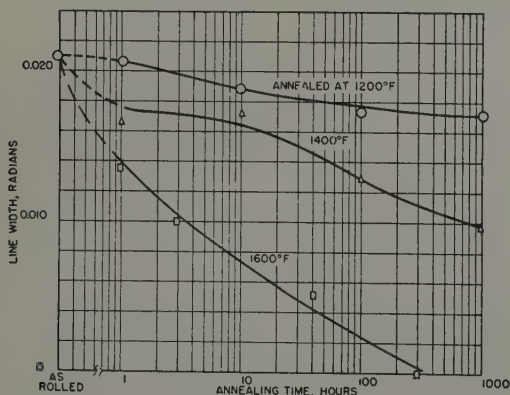


Fig. 6—Effect of annealing on width of (220) line of solution-treated low carbon N-155 alloy reduced 40 pct at 80°F.

complete after 1000 hr at 1600°F. It was completed at 1800°F in less than 10 hr. The recrystallized texture was of the same general type as existed before recrystallization.

Fig. 5 is typical of the effects of annealing on the (220) line width of all stock reduced 15 pct at temperatures from 80° to 1400°F. Similar results were had for the stock rolled 5 pct at 80°F—line widths of course being at correspondingly lower values, for the same annealing times and temperatures. Reduction of the (220) line widths may be interpreted as the result of internal stress relaxation during the annealing process. It should also be emphasized that this reduction is a recovery phenomenon occurring before recrystallization as the microstructural examination of annealed samples showed.

Comparison of Fig. 6, indicating the effects of annealing on the (220) line of the material rolled 40 pct at 80°F with Fig. 5 shows that 40 pct reduction resulted in significant line sharpening at 1200°F while 15 pct reduction did not. Apparently, the greater the magnitude of the internal stress, the

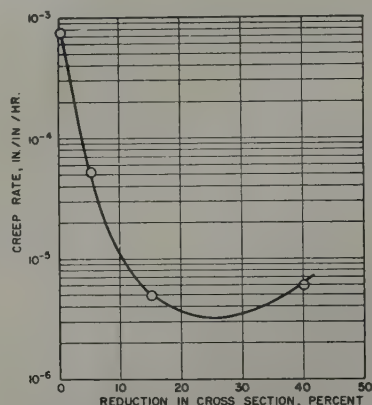


Fig. 7—Effect of reduction at 80°F on creep rates of solution-treated low carbon N-155 alloy under 50,000 psi at 1200°F.

lower the temperature at which effective relaxation occurs. This reduction of stability of the cold-worked structure with greater degree of cold working seems well substantiated by other investigators of recrystallization phenomena.

### Effects of Cold Working on Creep Resistance

Fig. 7 shows a maximum amount of creep resistance with reduction of the order of 25 pct and that further reduction resulted in either no further improvement of creep resistance or possibly an actual reduction. These results probably hold only for temperatures near 1200°F and in all probability would change for other temperatures of creep testing.<sup>4</sup> While this maximum effect of rolling on creep resistance was present, Fig. 2 indicates essentially that the internal stresses continued to increase with amount of rolling to at least 40 pct reduction.

Fig. 8 shows that the temperature of reduction had small effect on creep resistance under the conditions of testing at 1200°F, unless rolling temperatures greater than about 1500°F were used. For rolling temperatures greater than this, the creep resistance dropped off sharply. Fig. 4 indicates that this drop in creep resistance corresponded closely with the drop in line width.

Fig. 9 shows a typical relationship between creep resistance and annealing. Practically identical results were obtained for material rolled 15 pct at



1400°F. Creep rates for any given anneal after 5 pct reduction at 80°F were somewhat higher than those shown on Fig. 9, while creep rates for the material reduced 40 pct at 80°F were roughly similar for any given anneal to those on Fig. 9.

When comparison of the creep data obtained from the annealed samples was made with the line width data obtained from samples given the same anneal, it was apparent that a correlation between creep rate and line width might exist, but with the creep rate decreasing very rapidly with decreasing line width. This was also evident from comparison of the data on Figs. 3 and 4.

With this in mind, a correlation of the logarithm of the creep rate and the line width for both rolled, and rolled and annealed samples was tried with the result shown on Fig. 10. Considering the possible errors in measuring creep rates and line widths, most points fall no further off the mean line than could be accounted for by experimental error.

Some comment on the significance of this correlation can be made. If the Eyring reaction rate theory for creep is extended to include some average in-

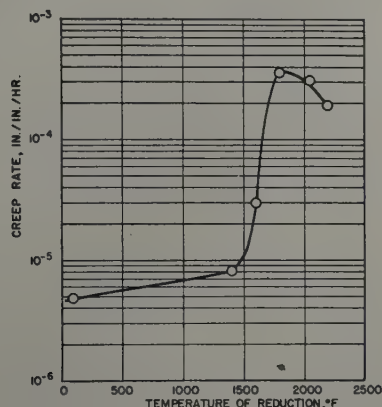


Fig. 8—Effect of rolling temperature on creep rate under 50,000 psi at 1200°F of solution-treated low carbon N-155 alloy reduced 15 pct.

ternal stress, the correlation shown on Fig. 10 can be predicted.

The appropriate expression from the theory for metallic creep appears to be:

$$\dot{\epsilon} = \text{constant}_1 \times T \times e^{-\frac{\Delta F}{RT}} \sinh \frac{\text{constant}_2 \sigma}{RT} \quad [1]$$

where  $\dot{\epsilon}$  is the creep rate at temperature  $T$  and stress  $\sigma$ ,  $\Delta F$  the free energy for activation of the fundamental unit of creep, and  $R$  the gas constant. When considering materials with internal stresses, satisfaction of equilibrium conditions results in the stresses appearing in regions of positive and negative sense. Thus in alternating regions the sense of the internal stress will be opposite to the sense of the applied stress and in the remaining regions it will be the same. However, if one assumes that the periodicity of these alternating stresses meets certain requirements,<sup>8</sup> the regions of internal stress opposite to the sense of the applied stress will control the creep rate. For these regions eq 1 becomes:

$$\dot{\epsilon} = \text{constant}_1 \times T \times e^{-\frac{\Delta F}{RT}} \sinh \text{constant}_2 \left( \frac{\sigma - \bar{\sigma}_i}{RT} \right) \quad [2]$$

when  $\bar{\sigma}_i$  is the effective internal stress. For a series

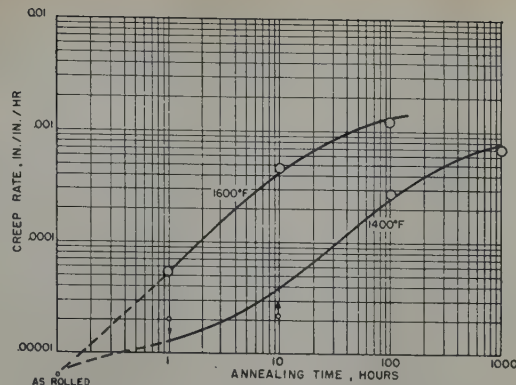


Fig. 9—Effect of annealing on secondary creep rate at 50,000 psi and 1200°F of solution-treated low carbon N-155 bar stock reduced 15 pct at 80°F.

of tests at constant  $T$  and  $\sigma$ , but with varying  $\bar{\sigma}_i$ , eq 2 can be rewritten:

$$\log \dot{\epsilon} = \text{constant}_3 - \text{constant}_4 \times \bar{\sigma}_i \quad [3]$$

Assuming a linear relation between  $\bar{\sigma}_i$  and the line width as measured herein, this is the relationship appearing on Fig. 10.

There are difficulties, however, in selecting from line broadening data an average internal strain and in turn converting this to an average internal stress. What half-height width of a line represents in terms of some average internal stress is not known, without further analysis of the broadened lines and other assumptions.<sup>1</sup> Even the correction for instrumental broadening using Warren's method is dependent upon an assumption as to the shape of the broadened lines, which assumption imperfectly represents the facts in this case. One is forced therefore, to conclude that the quantitative theoretical significance of Fig. 10 is limited at the present time, although qualitatively it indicates the relationship between internal stress and creep resistance.

The point (3) for the material reduced 40 pct at room temperature fell far off the correlation of Fig. 10. The observed creep rate of this material was too high for the measured line width. Further, the data of Fig. 6 showed that the (220) line width of this material (and this material only) was reduced appreciably during annealing at 1200°F. The conclusion is that reductions of the order of 40 pct on low carbon N-155 in the cold-working range resulted in appreciable relaxation of internal stresses at temperatures as low as 1200°F, such relaxation occurring during the creep test at this temperature. This limits the amount of reduction, and internal stress formation, that is useful for service at 1200°F, as shown in Fig. 7. Further, the line width that should have been entered on the correlation of Fig. 10 was some average line width which existed during the creep test at 1200°F. All other samples for which the data lie on the correlation of Fig. 10 had structures stable enough at 1200°F after rolling and/or annealing that the line widths measured before testing were substantially those existing during the creep test at 1200°F.

The factors explained above, which limited the amount of cold reduction that was useful in improving creep resistance of low carbon N-155 at 1200°F to about 40 pct, can be generalized somewhat with the aid of data published by Zschokke.<sup>4</sup> Zschokke found on another austenitic steel that there was a maximum benefit from cold working similar in na-

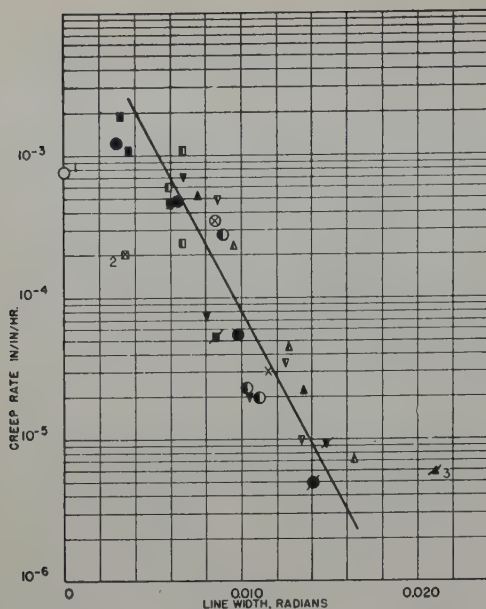


Fig. 10—Correlation of creep rate at 50,000 psi and 1200°F with (220) width of solution-treated, "cold" worked and annealed low carbon N-155 alloy.

ture to the results shown in Fig. 7. There appears to exist therefore, a critical amount of cold work beyond which relaxation of the internal stresses will occur to such an extent at the temperature of test or service considered that a maximum value for internal stresses effectively exists at each such temperature. Further, Zschokke found that the amount of cold work which gave the maximum effect decreased with increasing creep test temperature. This may be explained by saying that the temperature at which relaxation occurs to any appreciable extent is reduced as the amount of cold working is increased.

The materials reduced 15 pct at either room temperature or 1400°F were similar in every respect in regards to the interrelation between line width or internal stress and creep resistance either before or after annealing. Further, the results shown on Fig. 4 indicate that internal stresses after reductions of 15 pct are also the same up to temperatures of reduction of the order of 1500°F. Beyond this point relaxation during the rolling operation occurs. Since it is the internal stresses which improve creep resistance, it can be said that the temperature of "cold work" is immaterial as far as creep resistance is concerned over the temperature range, 80° to 1500°F.

The data for material rolled at 2200°F and the as-solution-treated material also did not fall on the correlation of Fig. 10 (points 1 and 2). Further, Fig. 8 showed that within the temperature range 1800° to 2200°F a rather curious reversal in creep resistance occurred. In view of the above, it seems that the creep resistance for material rolled in the vicinity of 2200°F and the solution-treated material was abnormally high, if internal stress control as exemplified by Fig. 10 is considered normal. No fundamental explanation of this phenomenon appears possible at the present time. However, from a technological standpoint the finding is important since the conclusion is that rolling of solution-treated N-155 at temperatures in the vicinity of 2200°F resulted in material which had better creep resistance than other "hot" worked materials.

Key to Symbols Used in Fig. 10

| Reduction (percent) | Temperature of Reduction (°F) | Temperature of Annealing (°F) | Symbol |
|---------------------|-------------------------------|-------------------------------|--------|
| 0                   | -                             | -                             | ○      |
| 5                   | 80                            | -                             | ■      |
| 5                   | 80                            | 1400                          | □      |
| 5                   | 80                            | 1600                          | ■      |
| 13                  | 80                            | -                             | ▲      |
| 13                  | 80                            | 1400                          | ●      |
| 13                  | 80                            | 1600                          | ●      |
| 10                  | 80                            | -                             | ▲      |
| 10                  | 80                            | 1400                          | ▲      |
| 10                  | 80                            | 1600                          | ▲      |
| 15                  | 1400                          | -                             | ▲      |
| 15                  | 1400                          | 1400                          | ▼      |
| 15                  | 1400                          | 1600                          | ▼      |
| 15                  | 1600                          | -                             | ×      |
| 15                  | 1800                          | -                             | ⊗      |
| 15                  | 2200                          | -                             | ■      |

## Conclusions

1—Cold working improves the creep resistance of low carbon N-155 and probably other alloys of the same general type through the presence of elastic stresses left in the lattice after the working operation.

2—For any given reduction, the optimum improvement in creep resistance can be had with any temperature of reduction below that which will allow relaxation of the internal stresses to a marked degree during the working operation itself. For reductions of 15 pct on low carbon N-155 alloy, this useful working temperature range is from 80° to 1500°F.

3—Conversely, increasing amounts of cold working give increasing creep resistance only up to the point where the internal stresses are so high as to permit relaxation to occur in significant amount at the particular service temperature being considered. It further appears that the critical amount of cold reduction decreases as the service temperature is raised. With low carbon N-155 for service or test at 1200°F, the critical cold reduction is approximately 25 pct.

4—A correlation of the logarithm of creep rate against internal stress as measured by diffraction line width existed for solution-treated and cold-rolled low carbon N-155 either with or without subsequent anneals. The full quantitative theoretical significance of this correlation must await more exact interpretation of broadened diffraction lines, although qualitatively it agrees with predictions from the Eyring reaction rate theory for creep.

## Acknowledgment

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# Thermal Variation of Young's Modulus in Some Fe-Ni-Mo Alloys

by M. E. Fine and W. C. Ellis

WHEN certain binary Fe-Ni alloys are worked cold and then stabilized by a stress-relief anneal, their Young's moduli are nearly invariant over a substantial temperature range determined by composition and work-anneal history.<sup>1</sup> In the present investigation addition of molybdenum to such alloys (besides increasing the yield strength) was found to diminish the sensitivity of the thermal coefficient of Young's modulus to composition changes. Such alloys are of interest for applications requiring a metal with controlled, low temperature coefficient of Young's modulus and substantial magnetic permeability.<sup>2</sup>

Young's modulus ordinarily decreases with rising temperature. In ferromagnetic alloys a change in modulus on heating due to loss of ferromagnetism modifies the temperature dependence. Far below the Curie temperature ferromagnetism alters the modulus in two ways: a—Addition of the energy of magnetization, a function of interatomic distance, changes the relation between interatomic energy and distance.<sup>1</sup> This lowers the modulus in the Fe-Ni and Fe-Ni-Mo alloys of this investigation. b—An applied stress changes the ferromagnetic domain arrangement so that linear magnetostriction contributes to the strain and further lowers the modulus.<sup>3</sup> Since in the alloys of this investigation both effects lower the modulus, loss of ferromagnetism on heating changes the slope of the modulus-temperature curve in a positive direction. With increasing temperature the slope of the modulus-temperature curve, due to progressive loss of ferromagnetism, becomes less negative, goes through zero (the modulus is minimum), becomes positive, and resumes its normal negative value above the Curie temperature.<sup>1</sup> The increase in modulus and decrease in curvature in the modulus-temperature curve occurring on work hardening have been attributed to a reduction in effect (b).<sup>1,3</sup> In the absence of ferromagnetism work hardening through introduction of residual strains would be expected to decrease the modulus.<sup>4</sup>

## Alloy Preparation—Test Methods

Four series of alloys having nominal molybdenum contents of 5, 7, 9, and 10 pct and containing 47 to 58 pct Fe (the analyzed compositions are given in Table I) were melted in air and cast as bars weighing from 2 to 6 lb. The charge consisted of electrolytic nickel, Armco iron, molybdenum (99+ pct) or ferromolybdenum (62 pct Mo), manganese, and aluminum as a deoxidizer. The bars were swaged cold to the desired diameters with intermediate anneals. Alloys in this composition range are reported<sup>5</sup> to be face-centered cubic and ferromagnetic at room temperature. The Curie temperatures<sup>5</sup> decrease with molybdenum. For example, keeping the Ni/Fe ratio at unity and increasing the molybdenum from 0 to 17 pct decreases the Curie tempera-

ture from approximately 500°C to room temperature. (The 17 pct Mo alloy requires quenching to retain a single phase.<sup>5</sup>)

Young's modulus at a series of temperatures from -50° to 100°C was determined by a dynamic method previously described.<sup>1,6</sup> In this method Young's modulus is calculated from the resonant frequency (in this case approximately 50,000 cycles per second) of a rod sample (approximately 2 in. long) vibrating longitudinally in the first mode. The densities of the samples at room temperature, Table I, were determined by the standard method of weighing in air and reweighing in redistilled bromobenzene. The linear coefficients of expansion, Table I, needed to calculate the sample length and density at the temperature of measurement, were obtained by observing the change in length (22° to 100°C) of an 8 in. gage distance with a two microscope cathetometer. The values of density and coefficient of expansion in the few samples checked are independent of treatment to the accuracy reported. This was assumed to be general for all the samples. The modulus values are accurate to  $\pm 0.05 \times 10^{11}$  dynes per sq cm. However, values of thermal change in modulus are accurate to  $\pm 0.005 \times 10^{11}$  dynes per sq cm.

## Young's Modulus

Values at 25°C: The modulus values of 0<sup>1</sup>, 5, and 10 pct Mo alloys at 25°C are plotted in Fig. 1 as functions of nickel. After working cold, the samples were either recrystallized at 950° to 1000°C or given a low temperature stabilizing anneal at 400°C. The 400°C anneal does not reduce the hardness nor cause recrystallization. Annealing at 400°C does

Table I. Compositions, Densities, and Coefficients of Expansion of Fe-Ni-Mo Alloys

| Sample<br>Design. | Chemical Composition,<br>Weight Pct |      |      |      |      |      |      | Dens-<br>ity,<br>G<br>per<br>cc | Mean<br>Linear<br>Co-<br>effi-<br>cient<br>of<br>Ex-<br>pansion<br>$\frac{1}{l} \frac{\Delta l}{\Delta T} \times 10^6$ |
|-------------------|-------------------------------------|------|------|------|------|------|------|---------------------------------|------------------------------------------------------------------------------------------------------------------------|
|                   | Mo                                  | Ni   | Fe   | Mn   | Co   | Al   | C    |                                 |                                                                                                                        |
| 6799              | 5.2                                 | 38.4 | 56.1 | 0.18 |      |      |      | 8.27                            | 4.5                                                                                                                    |
| 6800              | 5.3                                 | 40.2 | 53.9 | 0.27 | 0.35 | 0.01 |      | 8.28                            | 4.4                                                                                                                    |
| 6801              | 5.3                                 | 41.7 | 52.6 | 0.34 |      |      |      | 8.29                            | 6.0                                                                                                                    |
| 6837              | 5.2                                 | 43.5 | 50.6 | 0.42 |      |      |      | (8.30)                          | (8)                                                                                                                    |
| 6838              | 5.2                                 | 43.4 | 50.6 | 0.48 | 0.47 | 0.08 |      | (8.30)                          | (8)                                                                                                                    |
| 6882†             | 7.1                                 | 39.4 | 52.5 | 0.55 |      |      |      | (8.32)                          | (7)                                                                                                                    |
| 6883†             | 7.0                                 | 40.4 | 51.5 | 0.58 |      |      |      | 8.32                            | (7)                                                                                                                    |
| 6884†             | 7.2                                 | 41.5 | 50.3 | 0.61 |      |      |      | (8.32)                          | (7)                                                                                                                    |
| 6892*             | 8.8                                 | 40.6 | 49.4 | 0.64 |      |      | 0.02 | 8.37                            | (8)                                                                                                                    |
| 6902*             | 9.2                                 | 38.6 | 51.2 | 0.49 |      |      |      | 8.36                            | (8)                                                                                                                    |
| 6903*             | 9.1                                 | 39.7 | 50.1 | 0.61 |      |      |      | (8.36)                          | (8)                                                                                                                    |
| 6904*             | 8.9                                 | 41.6 | 48.4 | 0.62 |      |      |      | 8.37                            | (8)                                                                                                                    |
| 6906*             | 9.2                                 | 41.7 | 47.9 | 0.45 |      |      |      | (8.37)                          | (8)                                                                                                                    |
| 6907*             | 9.0                                 | 40.6 | 49.2 | 0.55 |      |      |      | (8.37)                          | (8)                                                                                                                    |
| 6908*             | 9.1                                 | 41.3 | 48.5 | 0.48 |      |      |      | (8.37)                          | (8)                                                                                                                    |
| 6909*             | 9.5                                 | 42.7 | 46.6 | 0.57 |      |      |      | 8.40                            | (8)                                                                                                                    |
| 6802              | 10.2                                | 36.1 | 53.4 | 0.11 |      |      |      | (8.40)                          | 8.5                                                                                                                    |
| 6803              | 10.7                                | 38.4 | 50.5 | 0.13 | 0.37 | 0.01 |      | 8.42                            | 8.5                                                                                                                    |
| 6804              | 10.8                                | 40.1 | 48.7 | 0.17 |      |      |      | 8.43                            | (8)                                                                                                                    |
| 6805              | 9.8                                 | 42.8 | 47.1 | 0.20 |      |      |      | 8.43                            | 8.0                                                                                                                    |

\* 7 lb melts using ferromolybdenum.

† 7 lb melts using 99+ Mo.

Balance are 2 lb melts using 99+ Mo.

Values in parentheses were interpolated from the measured values.

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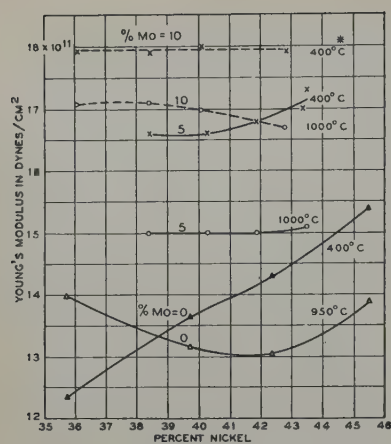


Fig. 1—Young's modulus in Fe-Ni-Mo alloys at 25°C.

Previous to annealing, the binary alloys were swaged cold 74 pct from an initial diameter of 0.390 in.; the ternary alloys, 41 pct from 0.260 in. In the 5 pct Mo series, the molybdenum contents varied from 5.2 to 5.3 pct; in the 10 pct series, from 9.8 to 10.8 pct.

\*Annealing temperature. All annealing times were 1 hr.

$$\frac{1}{\text{cm}^2} = 1.4504 \times 10^{-5} \text{ psi.}$$

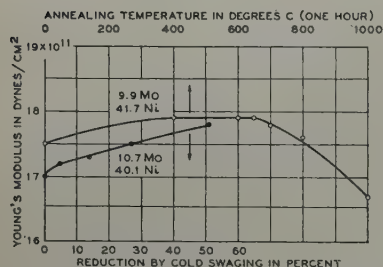


Fig. 2—Effect of annealing temperature and cold reduction on Young's modulus of two 10 pct Mo alloys.

Upper curve—alloy was initially cold reduced 41 pct from 0.260 in. diam. Lower curve—alloy was cold reduced indicated percentage from 0.210 and annealed at 400°C for 1 hr before testing. Temperature of test, 25°C.

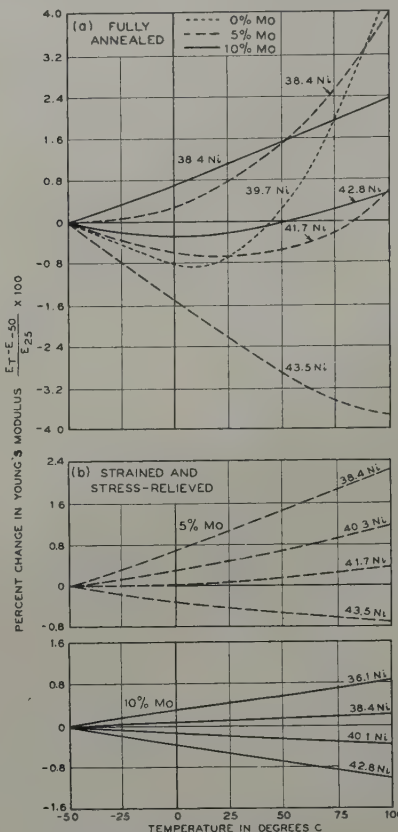
relieve residual strains to the extent that subsequent heating to 100°C provides insufficient thermal energy to promote further relaxation.

Young's modulus depends on both composition and the state of strain in the alloy. The addition of molybdenum progressively raises the modulus of alloys in corresponding states of strain. Molybdenum additions, furthermore, render the modulus less sensitive to change in nickel content. The theory of the effect of molybdenum on the modulus is discussed in a later section.

In all the alloys of Fig. 1, except 35.7 pct Ni-Fe,<sup>1</sup> the presence of work hardening increases Young's modulus as shown by comparison of the curves for the 400° and 1000°C anneals (due to a decrease in the stress-produced linear magnetostriction). The effect of cold reduction was studied in more detail in a 10.7 pct Mo, 40.1 pct Ni alloy, lower curve, Fig. 2. The modulus in this alloy increases almost uniformly with the amount of cold reduction. In the upper curve of Fig. 2 annealing temperature (9.9 pct Mo, 41.7 pct Ni alloy) is the variable; the initial cold reduction is kept constant. As the annealing temperature is increased the modulus at first increases, due to stress relief, and then de-

Fig. 4 (right)—Percentage thermal variation of Young's modulus in cold-worked and stress-relieved 7 and 9 pct Fe-Ni-Mo alloys.

Cold swaged from 0.300 to 0.200 in. diam. (56 pct). Annealed 1 hr at 500°C. An annealing temperature of 500°C was chosen instead of 400°C (Fig. 3b) because in the Fe-Ni-Mo alloys annealed 1 hr at 400°C the modulus increased slightly during a two week treatment at 150°C.





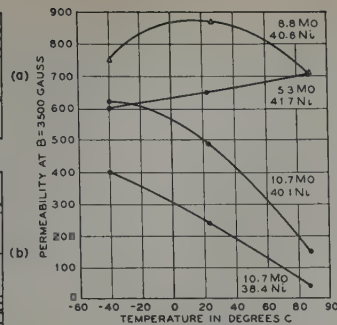
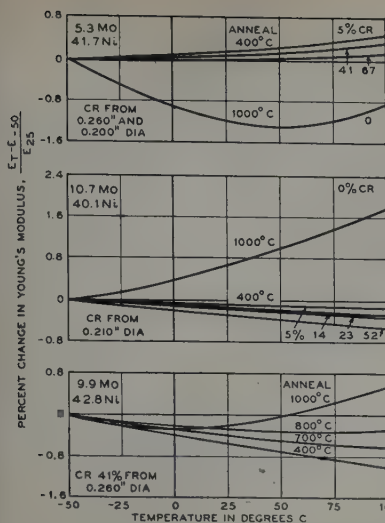


Fig. 6 (left)—Percentage thermal change in Young's modulus as affected by variation in degree of cold work and annealing temperature.

CR (cold reduced) refers to reduction in cross-sectional area.

Fig. 7 (left)—Permeabilities of some Fe-Ni-Mo alloys.

● — Cold reduced 41 pct from 0.260 in. diam and annealed 1 hr at 400°C.  
 Δ — Cold reduced 56 pct from 0.300 in. diam and annealed 1 hr at 500°C.  
 The permeabilities of the 8.8 pct Mo alloy are higher than the 5.3 and 10.7 pct Mo alloys because the former was annealed at a higher temperature.

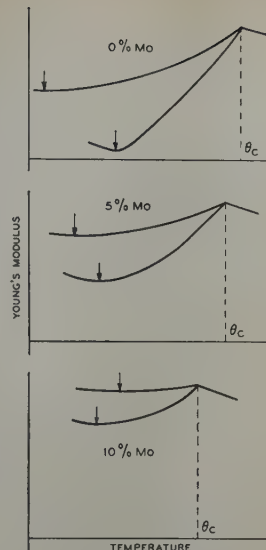


Fig. 8 (right)—Effect of increasing molybdenum on the modulus-temperature curve.

Upper curves—work hardened condition. Lower curves—fully annealed condition. Arrows indicate minima in modulus-temperature curves.

of the Curie temperature, a function of composition. Consistent with the dependence of the Curie temperature on nickel and molybdenum, the temperature of minimum modulus (predicted from the observed slopes in the  $-50^{\circ}$  to  $100^{\circ}\text{C}$  range) increases with nickel content and decreases with molybdenum content. The effects of molybdenum and nickel are interrelated; for a minimum modulus at room temperature the ratio of nickel to iron increases from 0.7 to 0.9 as the molybdenum is increased from 0 to 10 pct.

The curvature in the modulus change-temperature curves (Fig. 3a) about the temperature of minimum modulus decreases on adding molybdenum. (Compare the data for the 0, 5, and 10 pct Mo alloys whose minima are in the temperature range of test). Furthermore, the slopes at temperatures considerably removed from the minimum modulus become numerically less as molybdenum is added.

Cold working of binary Fe-Ni alloys causes the modulus change-temperature curves to be shallower at their minima.<sup>1</sup> Moreover, the slope changes much more gradually at temperatures considerably removed from the minimum. In cold-worked alloys, the presence of the molybdenum to some extent further reduces the curvature in the region of the minimum, but its principal effect is to decrease the sensitivity of the temperature coefficient of modulus to change in nickel content. The evidence for this is in the modulus change-temperature curves for the cold-worked condition (stabilized by a stress-relief anneal at  $400^{\circ}$  or  $500^{\circ}\text{C}$ ) shown in Figs. 3b and 4; the curves fan out less from varying nickel as the molybdenum content is increased. The same effect is illustrated more directly in Fig. 5, showing the mean thermal coefficient of modulus in 0, 5, 7, 9, and 10 pct Mo alloys between  $-50^{\circ}$  and  $100^{\circ}\text{C}$  (slopes of the curves in Fig. 3b and 4). The major effect is for molybdenum contents of more than 5 pct. Adding 9 or 10 pct Mo diminishes the sensitivity of the coefficient to variations in Fe-Ni ratio by a factor of two.

Adding nickel increases the temperature of minimum modulus in both cold-worked and fully annealed alloys. The effect of molybdenum is not so simple. Adding molybdenum to fully annealed alloys decreases the temperature of minimum, but in cold-worked alloys adding molybdenum increases the temperature of minimum modulus. The temperature of minimum in cold-worked binary Fe-Ni

alloys is less than in fully annealed alloys. As molybdenum is added the temperatures of minimum for the two conditions approach each other, are equal at approximately 7 pct Mo, and in 10 pct Mo alloys the temperature of minimum is higher for the cold-worked condition (compare Fig. 3a and 3b). This observation has theoretical significance and will be discussed later in the paper.

The effects of cold working were investigated in more detail in two alloys. The results are shown in Fig. 6a and 6b. The samples were first fully annealed at  $1000^{\circ}\text{C}$  and then cold worked the percentages shown in the figure (followed by a stabilizing anneal at  $400^{\circ}\text{C}$ ). The initial amounts of cold work produce the greatest effect in flattening and shifting the minimum. This suggests that the principal changes effected by cold work are not due to texture development, since such small amounts of cold work would hardly be expected to develop preferred orientations. These figures again show the opposite effect of the presence of cold work in shifting the minimum in the 5 and 10 pct Mo alloys. The initial cold reduction decreases the temperature of minimum in the former, Fig. 6a, but increases the temperature of minimum in the latter, Fig. 6b. Subsequent cold reduction in both cases decreases the thermal coefficient of modulus.

The effect of change in annealing temperature on the modulus-temperature relation in a 10 pct Mo alloy was studied in detail, Fig. 6c. Increasing the annealing temperature from  $400^{\circ}$  to  $1000^{\circ}\text{C}$  decreases the temperature of minimum from well above  $100^{\circ}\text{C}$  to approximately  $0^{\circ}\text{C}$ ; the slope becomes more positive. Comparing the curves for the  $800^{\circ}$  and  $1000^{\circ}\text{C}$  anneals at their minima, the latter has more curvature.

The effects of cold work and annealing temperature on the temperature of minimum modulus (Fig. 6b and 6c) are mutually consistent. The largest effect of cold work occurs for small cold reductions; the largest effect of annealing is for removal of the last residual strains introduced by the working ( $800^{\circ}$  to  $1000^{\circ}\text{C}$ ). Decrease in temperature of anneal (less removal of strain) has the same effect as increase in strain by cold work.

When the final annealing temperature is constant, the modulus and the thermal variation in modulus depend principally upon the amount of cold reduction after the last full anneal; however, the modulus and thermal variation in modulus depend to some



extent on the working and annealing procedure before the last full anneal. This is not unusual for a property depending upon the state of internal strain.

### Magnetic Permeability and Mechanical Strength

Properties of associated importance with the modulus characteristics are the magnetic permeability and the strength. Permeabilities for some alloys are shown in Fig. 7. The thermal permeability variation (at 3500 gauss) is principally due to the decrease in Curie temperature as molybdenum is added. In a 10.7 pct Mo, 38.4 pct Ni alloy cold worked and stress relieved at 400°C, the permeability falls to a low value at 85°C indicating the Curie temperature is not much higher. The permeability of an 8.8 pct Mo, 40.6 pct Ni alloy stress relieved at 500°C remains between 700 and 900 for the temperature variation, -40° to +85°C. The permeabilities are higher in this latter alloy because the annealing temperature is higher.

The strengths of Fe-Ni alloys are substantially increased by addition of molybdenum. For example, an alloy containing 8.9 pct Mo and 41.6 pct Ni, cold worked 56 pct and stress-relief annealed at 500°C has a proportional limit of 115,000 psi. An Fe-Ni alloy containing 45 pct Ni after similar treatment has a proportional limit of 50,000 psi. The ultimate tensile strength of the molybdenum containing alloy is 148,000 psi and the elongation in 2 in. is 2 pct.

### Theory of Effect of Mo on the Modulus

Addition of molybdenum to Fe-Ni alloys modifies the modulus through its effects on ferromagnetism and interatomic binding energy. Ferromagnetism, responsible for the observed unusual temperature variation of modulus in Fe-Ni and Fe-Ni-Mo alloys, as previously stated, changes the modulus directly through addition of the energy of magnetization term to the interatomic binding energy. Furthermore, the stress-produced linear magnetostriction increases the strain and lowers the modulus. In the following discussion the former will be referred to as effect (a) and the latter effect (b).

The modulus as it varies with temperature in a 0, 5, and 10 pct Mo alloy (approximately 42 pct Ni) is shown schematically in Fig. 8. The upper curve of each set is for work-hardened alloys, the lower for well-annealed alloys. In the temperature range -50° to 100°C these curves were constructed from actual data. The approximate behavior over a considerably wider temperature range can be deduced from room temperature measurements, since reducing the nickel lowers the Curie temperature and is approximately equivalent to lowering the temperature of test. The curves for the two alloy conditions are shown coming together at the Curie temperature. Actually this may not happen due to the effects of internal strain and crystal orientation on the modulus. To a first approximation the lowering of the upper curve from a straight line extrapolated from above the Curie temperature is due to effect (a); the difference between upper and lower curves is due to effect (b).

Addition of molybdenum, which increases the mechanical strength, by obstructing domain movement reduces the stress-produced linear magnetostriction (b). This partially causes the increase in modulus and decrease in curvature in the modulus-temperature curve on adding molybdenum to well-annealed alloys (Figs. 1 to 3 and 8). Effect (b) increases in magnitude, Fig. 8, over a limited temperature range on heating as in nickel<sup>7</sup> probably because

domain movement becomes easier as the temperature is raised.

Effect (a), as molybdenum is increased, diminishes in magnitude and the minimum due to it nears the Curie temperature. Hence, in 0 and 5 pct Mo alloys work hardening, that is, reducing effect (b), decreases the temperature of minimum in the modulus-temperature curve, but in 10 pct Mo alloys work hardening increases the temperature of minimum as shown by the arrows in Fig. 8. Confirming experimental evidence for a diminishing of effect (a) on adding molybdenum comes from expansion data: The coefficient of expansion increases on adding molybdenum, Table I, showing a decrease in the volume effect from loss of ferromagnetism. The decrease in volume effect implies that as molybdenum is added the interatomic distance corresponding to maximum energy of magnetization nears the nonferromagnetic interatomic distance.

### Summary

Young's modulus and its temperature coefficient were investigated in low coefficient Fe-Ni-Mo alloys under varying conditions of working and annealing. In the ternary as well as the binary Fe-Ni alloys, the temperature interval of nearly constant Young's modulus is greatly extended by work hardening. A stress-relief anneal is necessary to stabilize the alloys. Addition of 9 or 10 pct Mo decreases the sensitivity of the thermal coefficient to variations in nickel by approximately a factor of two. In these alloys the mean thermal coefficient of modulus for the temperature range -50° to 100°C varies from +50 to  $-50 \times 10^{-6}$  degree C<sup>-1</sup> as the nickel varies from 36.5 to 41.5 pct.

An alloy containing 9 pct Mo, 38 to 41.5 pct Ni, and balance Fe in the cold-worked condition has a low temperature coefficient of Young's modulus, substantial magnetic permeability reasonably constant over a limited temperature range, and high strength. The coefficient of modulus can be controlled by controlling the Fe-Ni ratio. A further measure of control can be exercised by varying the straining-annealing procedure.

The principal effects of molybdenum on the temperature dependence of modulus are explained by assuming that molybdenum decreases the modification in the interatomic energy-interatomic distance relation from the energy of magnetization.

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# Effect of Rate of Cooling on the Alpha-Beta Transformation in Titanium and Titanium-Molybdenum Alloys

by Pol Duwez

The effect of the rate of cooling on titanium, zirconium, and thallium has been measured. For titanium-molybdenum alloys, it has been shown that for molybdenum concentration up to 8 pct the rate of cooling has no effect on the transformation temperature, but this temperature decreases progressively with increasing molybdenum content.

HIGH-strength to weight ratio and remarkable corrosion resistance have often been advanced as the main reasons for the present widespread interest in titanium. For the physical metallurgist, the existence of an allotropic transformation in titanium is another important factor. As in the case of iron, an allotropic transformation may be the fundamental property upon which the response of Ti-base alloys to heat treatment will depend. It is therefore important to study the mechanism of the allotropic transformation in pure titanium and the effect of alloying elements on this transformation.

The existence of an allotropic transformation in titanium was reported in 1931 by Schulze.<sup>1</sup> Later, De Boer et al.<sup>2</sup> determined the transformation temperature from a discontinuity in the electrical resistivity at  $882^{\circ}\pm 20^{\circ}\text{C}$ . According to recent work,<sup>3</sup> the transformation temperature is  $882.5^{\circ}\pm 1^{\circ}\text{C}$ . The crystal structure of the room temperature  $\alpha$  phase is hexagonal close-packed and the high temperature  $\beta$  phase is body-centered cubic.<sup>4</sup>

It is well known that the high temperature  $\beta$  phase of pure titanium cannot be retained by quenching to room temperature. Several investigators<sup>5-7</sup> have shown that in alloys of titanium with metals which are soluble in the  $\beta$  phase (for example, nickel, molybdenum, chromium, or manganese), the  $\beta$  structure can be retained, providing the concentration of the alloying element is greater than a certain critical value. Below this critical value, the alloys transform during quenching, at least partially, into a supersaturated solid solution having the  $\alpha$  structure. This behavior is very similar to that

found in some iron binary alloys (Fe-Ni and Fe-Mn, for example) and is an indication that the transformation might occur by means of a shear mechanism analogous to that observed in the austenite-martensite reaction.

The present investigation is mostly concerned with the effect of the rate of cooling on the  $\beta$  to  $\alpha$  transformation. In the first portion of this paper, the results obtained on pure titanium are described. Two other pure metals, zirconium and thallium, were also investigated, because they both have an allotropic transformation like titanium, from an hexagonal close-packed to a body-centered cubic structure. For purposes of comparison, the effect of rate of cooling of the  $\gamma$  to  $\alpha$  transformation of iron was included in the experimental program. The second part of this paper deals with Ti-Mo alloys. The equilibrium phase boundaries involving the solid state reactions on the Ti-rich side of the system were determined and a study was made of the effect of the rate of cooling on the transformation of the high temperature  $\beta$  solid solution.

## Experimental Procedure

Since the main object of the present investigation was the determination of the effect of the rate of cooling on a transformation temperature, the best technique available was that used by Greninger<sup>8</sup> in his study of the martensite arrest in carbon steels. This method consists of heating a very small sample of metal to which fine thermocouple wires are attached, cooling the sample rapidly by means of a blast of helium, and recording the temperature vs. time curve on an oscillograph. The apparatus used in the present experiments was very similar to that described by Greninger, except that the heating coil was made of molybdenum wire (0.040 in. in diam) and the assembly was placed in a bell jar under vacuum of  $10^{-5}$  mm Hg or less. The specimen con-

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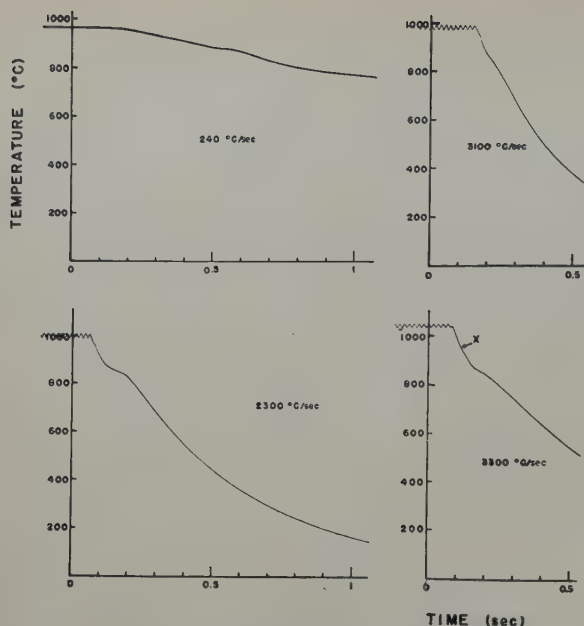


Fig. 1—Cooling curves obtained on pure titanium at various rates of cooling.

sisted of two pieces of metal about 0.020 in. thick and less than 1/16 in. square. The 0.005 in. chromel-alumel thermocouple wires were placed between the two pieces of metal and the assembly spot welded. In an effort to reduce contamination of titanium by any residual oxygen and nitrogen, the specimen was heated as fast as possible (between 5 and 10 sec) above the transformation temperature and immediately quenched. The temperature was recorded on a rotating drum type oscillograph (made by the William Miller Corp., Pasadena, Calif.). The galvanometer was a 65 cycle element, having a resistance of 45 ohms and a sensitivity of 1 in. deflection per 25 microamperes. The instrument was calibrated by means of a Leeds and Northrup portable precision potentiometer. Records were obtained with paper speeds of about 4½ and 8 in. per sec.

The Ti-Mo alloys were prepared by melting in a helium arc furnace. The furnace was very similar to that described in ref. 9, except that the top electrode, made of molybdenum, was water cooled. This electrode was designed so that the cooling water was brought to the tip of the electrode, leaving only 3/16 in. of molybdenum between the arc and the cooling water. The operation of the furnace was frequently checked by melting a specimen of pure titanium and measuring the Vickers hardness before and after melting. It was assumed that no contamination was introduced by melting when the average Vickers hardness number did not increase by more than 5 points.

The melting procedure consisted of loading the desired amount of molybdenum powder into a cavity drilled in a piece of titanium and covering the cavity with a titanium cap. The total weight of a specimen was between 5 and 15 g. Each specimen was melted several times in order to obtain an homogeneous alloy. The alloys were not chemically analyzed after melting. Several specimens, however, were weighed before and after melting and, since the change in weight was found to be less than 0.2 pct, it was assumed that the change in composition, if any, was negligible. After melting, the alloys that were sufficiently ductile (up to about 10 pct Mo) were cold rolled with various reductions in cross-

section. All the specimens, whether rolled or not, were sealed in evacuated fused silica tubes (vacuum of  $10^{-4}$  mm Hg or less) and homogenized for 24 hr at 982°C (1800°F). The specimens were then quenched in water from that temperature. All subsequent heat treatments were also carried on in evacuated fused silica capsules. All these heat treatments were made at constant temperature and followed by quenching.

For microscopic observation, the specimens were polished by conventional methods, finishing with 0 to 2 microns diamond powder and etching with a solution of one part 48 pct hydrofluoric acid, one part concentrated nitric acid, and two parts glycerine. A magnification of 250 times was used.

## Results of Measurements on Pure Metals

**Titanium:** Pure titanium obtained by the iodide process was received from the Foote Mineral Co. and from the New Jersey Zinc Co. A small piece of iodide titanium was also obtained from the Naval Research Laboratory through the courtesy of Dr. Chapin. The Vickers hardness (10 kg load) of any of these three specimens varied from about 55 to 75, this variation within a given sample being due probably to crystal orientation. Measurements of Vickers hardness therefore was not suitable for detecting possible differences in the degree of purity of the three samples.

A total of approximately 170 cooling curves was obtained with various rates of cooling ranging from 4° to about 15,000°C per sec. Typical cooling curves obtained with various rates of cooling are shown in Fig. 1. With the exception of a few tests, the break in the cooling curve at the transformation point was quite easy to locate and the accuracy of measurement of the transformation temperature was approximately  $\pm 4^\circ\text{C}$ .

The results of measurements on the three samples of iodide titanium are summarized in the graphs of Fig. 2. The scatter between transformation temperatures measured on several samples around a given rate of cooling seems to exceed  $\pm 4^\circ\text{C}$ , which is the estimated accuracy of measurement. It is probable that part of the scatter is due to the statistical nature of the nucleation process. In any case, all the measurements seem to be included in a band which has a width of about  $10^\circ\text{C}$  at low rates of cooling and of about  $20^\circ\text{C}$  at high rates. By taking the center line of such a band as an average curve, it may be concluded that the  $\beta$  to  $\alpha$  transformation of titanium decreases slightly with increasing rates of cooling and varies from 882°C at relatively low rates to about 850°C at cooling rates of the order of 10,000°C per sec.

In about half of the 170 cooling curves obtained for the pure titanium specimens, a more or less pronounced heat effect was observed at a temperature higher than that at which the main thermal arrest took place. In many cases a definite change in the slope of the cooling curve was noticeable, as shown at point X on one of the graphs reproduced in Fig. 1. The temperature at which this anomaly was observed varied from specimen to specimen, covering a range from 905° to about 960°C. The variation in the temperature at which the extra thermal arrest was observed excluded the possibility of a second allotropic transformation, although such a transformation has been suggested by McQuillan.<sup>10</sup>

In a more detailed investigation recently published,<sup>8</sup> this same author seems to refute his previous



conclusions and demonstrates that the anomalies observed in the behavior of titanium around the  $\alpha$ - $\beta$  transformation are due to contamination of the specimens by oxygen. In measuring the equilibrium pressure of hydrogen in contact with a titanium specimen as a function of temperature, McQuillan found that, on heating, the discontinuity in pressure is very sharp at the  $\alpha$ - $\beta$  transformation temperature (882.5°C). As the temperature is increased, however, the specimen seems to continue transforming up to (in one case) about 930°C and from there on the pressure-temperature relationship becomes normal (linear relation between  $\log p$  and  $1/T$ ). The explanation for the progressive transformation is that even in a vacuum as low as  $10^{-5}$  mm Hg, there is enough residual oxygen to contaminate the outside layer of the titanium specimen. It is therefore logical to expect that the uncontaminated part of the specimens (the inside core) will transform at 882.5°C with a sharp discontinuity in the pressure. The outside layer, which contains all concentrations of oxygen from zero to a maximum at the surface, will transform gradually over a range of temperatures corresponding to the range of oxygen concentration present. Upon cooling, the reverse mechanism takes place, and the same relationship is observed between the pressure and temperature. By introducing a very small amount of oxygen into the vacuum chamber in order to purposely contaminate the specimen, McQuillan observed that the range of temperature over which the transformation proceeds was increased, and in one case extended from 882.5° to about 960°C.

The conclusions reached by McQuillan concerning the effect of surface contamination on the transformation temperature of titanium clearly explain the anomalies found in the cooling curves discussed in the present study. The very thin specimen used in the quenching experiments is, of course, subject to some contamination by residual oxygen and nitrogen, even if, as stated above, the time necessary for heating the specimen is of the order of seconds only. The oxygen contaminated case around the specimen undergoes the  $\beta$  to  $\alpha$  transformation at temperatures above the normal transformation temperature and a decrease in the slope of the cooling curve is observed as shown at point X of Fig. 1. When the transformation temperature of pure titanium is reached, the uncontaminated core of the specimen transforms and the main thermal arrest appears on the cooling curve. Since the degree of contamination is not exactly the same from test to test, the first break in the cooling curve is sometimes more or less pronounced and sometimes absent. When the extra thermal arrest is actually observed, it is not always at the same temperature, but always within a range which is very nearly the same as that found by McQuillan (905° to 960°C).

Table I. Effect of Rate of Cooling on Transformation Temperature of Thallium

| Rate of Cooling,<br>°C per Sec | Transformation<br>Temperature, °C |
|--------------------------------|-----------------------------------|
| 105                            | 231                               |
| 650                            | 228                               |
| 950                            | 233                               |
| 1120                           | 229                               |
| 1500                           | 231                               |
| 2150                           | 229                               |
| 3000                           | 232                               |
| 8100                           | 230                               |

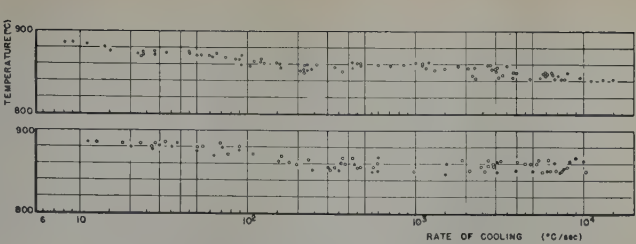


Fig. 2—Effect of rate of cooling on the allotropic transformation temperature of titanium (iodide process). Upper graph: Foote Mineral Co. titanium. Lower graph: ○—New Jersey Zinc Co. titanium. ●—Naval Research Laboratory titanium.

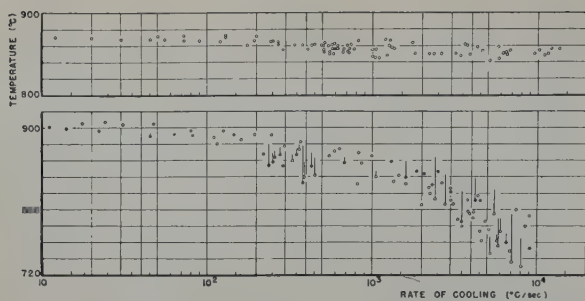
**Zirconium:** Because zirconium and titanium have very similar physical properties, it was anticipated that the effect of the rate of cooling on the  $\beta$  to  $\alpha$  transformation of zirconium would be the same as that found for titanium. About 85 cooling curves were recorded on zirconium specimens cut from a bar of pure zirconium made by the iodide process by the Foote Mineral Co. The results, shown in Fig. 3, indicate that the transformation temperature of zirconium decreases from 865° to about 850°C with increasing rates of cooling. The effect of rate of cooling is therefore smaller for zirconium (about 15°C) than for titanium (about 35°C).

It is interesting to mention that for zirconium no additional thermal arrest of the type found for titanium was observed on any of the cooling curves. Since the experimental conditions were the same for the two metals, it seems that either the rate of absorption of oxygen and nitrogen is smaller in zirconium than in titanium, or that the transformation temperature of zirconium is not greatly affected by oxygen and nitrogen. Since zirconium is generally considered as a better “getter” than titanium, the second hypothesis is probably the more likely one.

**Thallium:** Besides titanium and zirconium, thallium is the only other element having an allotropic transformation from a high temperature, body-centered cubic form to a low temperature, hexagonal close-packed form.<sup>11\*</sup> A few measurements were performed on 99.9 pct pure thallium obtained from Belmont Smelting & Refining Works, Brooklyn. The thermal arrest was not as pronounced as in the case of titanium and zirconium, due to the fact that the latent heat of transformation for thallium is only 0.074 kcal per mol compared with 0.71 for zirconium.<sup>12</sup> However, the arrest could be located easily and the accuracy in the temperature measurement was about  $\pm 4^\circ\text{C}$ . The results summarized in Table I indicate that up to a rate of cooling of about 8000°C per sec, the transformation temperature remains within the limits of accuracy of  $\pm 4^\circ\text{C}$ . It may be concluded therefore that if rates of cooling up to 8000°C per sec have any effect on the transformation temperature of thallium, this effect is less than about  $\pm 4^\circ\text{C}$ .

**Iron:** Although many studies have been published on the effect of the rate of cooling on the transformation in Fe-base binary alloys, the early results of Esser et al.<sup>13</sup> seem to be the only ones obtained on relatively pure iron and with high rates of cooling. According to these investigators, the  $\alpha$  to  $\gamma$  transformation can be depressed from 905°C to as low as about 500°C at cooling rates of the order of 10,000°C per sec. The only information on the carbon content of the material used by Esser is that it was less than 0.017 pct and no definite statement is made concern-

\* Since this work was completed, a body-centered cubic to hexagonal close-packed allotropic transformation has been found in hafnium; it will be described in a forthcoming paper.



○—Bureau of Standards iron. ●—National Research Corp. iron.  
Fig. 3—Effect of rate of cooling on the allotropic transformation temperature of zirconium (upper) and iron (lower).

ing other possible impurities. Since Esser's experiments were performed in an atmosphere of hydrogen, there might also be some question about the effect of hydrogen absorption on the allotropic transformation.

Since iron may be obtained at present with a higher degree of purity than at the time the work of Esser was reported, 1933, the effect of rate of cooling on the  $\gamma$  to  $\alpha$  transformation temperature was reinvestigated on two different iron samples. The first sample was a small bar of spectroscopically pure iron from the Bureau of Standards. The purity of this particular sample (ingot No. 8) has been described in ref. 14; the carbon content is less than 0.001 pct. The second kind of iron was a 10 lb vacuum-cast ingot purchased from National Research Corp., Boston, Mass. A typical analysis of this type of metal is less than 0.005 pct C, less than 0.02 pct O, less than 0.001 pct N and H, and traces of various metallic impurities (each less than 0.001 pct).

The effect of the rate of cooling on the  $\gamma$  to  $\alpha$  transformation is shown in Fig. 3 for the two types of iron tested. In approximately half of the cooling curves, a more or less pronounced recalescence took place at the transformation temperature. This behavior is indicated on the diagram of Fig. 3 by means of a vertical line connecting the minimum temperature corresponding to the beginning of transformation to the maximum temperature reached after recalescence. In spite of the relatively large scatter in experimental results, Fig. 3 indicates clearly that

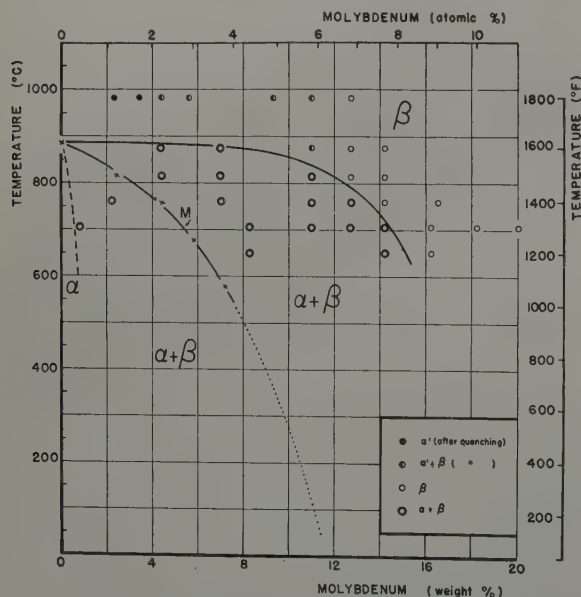
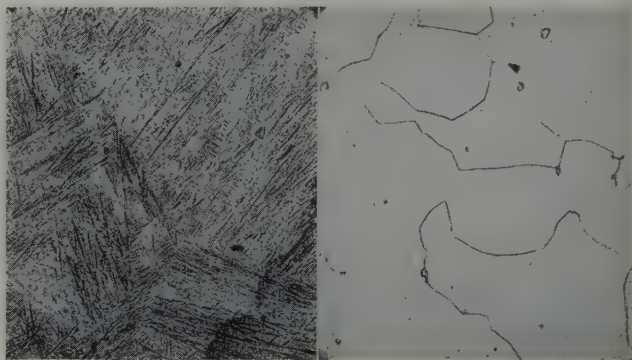


Fig. 4—Partial phase diagram of the Ti-Mo system. Curve M indicates the transformation temperature during quenching from the beta field.

by increasing the rate of cooling it is possible to decrease the allotropic transformation temperature of iron from 905°C to approximately 750°C at a cooling rate of about 10,000°C per sec. This decrease of the  $\gamma$ - $\alpha$  transformation temperature is much smaller than that reported previously by Esser et al.<sup>13</sup> The most probable reasons for the lack of agreement between the two investigations are, first, the difference in the purity of the iron samples, and second, the effect of hydrogen used as an atmosphere in Esser's experiments.

In any case, the rate of cooling has a greater influence on the  $\gamma$  to  $\alpha$  transformation temperature of iron than on the  $\beta$  to  $\alpha$  transformation temperature of titanium, zirconium, and thallium. In addition, recalescence was frequently observed in iron, but never occurred in any of the measurements made on the other three metals.

Results of thermal analysis measurements are difficult to interpret on a quantitative basis and therefore it is not possible to determine exactly the



10.85 pct Mo ( $\alpha'$ ). 12.7 pct Mo ( $\beta$ ).  
Fig. 5—Structure of Ti-Mo alloys quenched from 980°C.

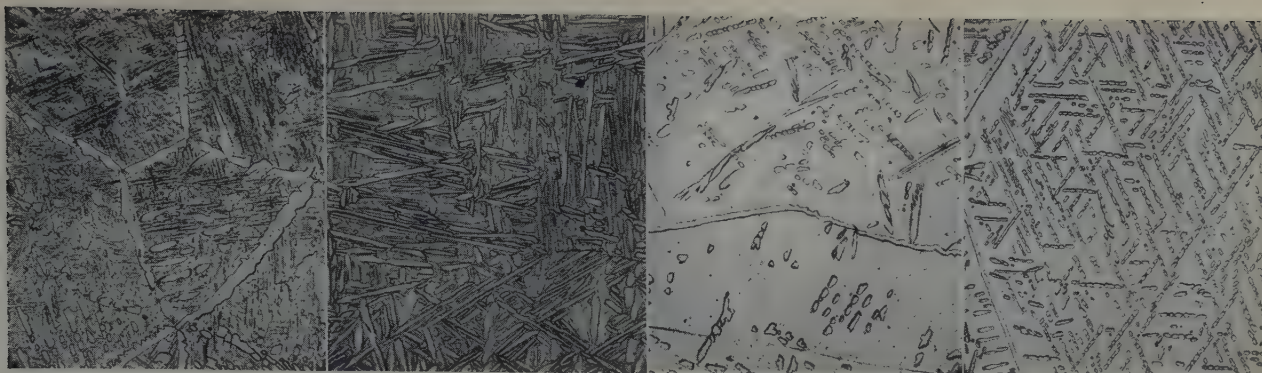
factors responsible for the differences between the behavior of titanium and that of iron. The change in crystal structure is of course a factor to consider. From this point of view, the results indicate that the rate of cooling has less effect on a body-centered cubic to hexagonal close-packed transformation than on a face-centered cubic to body-centered cubic transformation. This observation, however, does not lead to the conclusion that the atomic processes involved in titanium and in iron are necessarily different. In fact, both transformations are probably of the nucleation and shear type, and apparent lack of similarity in the behaviors of the two metals during fast cooling may simply be the result of differences in the numerical values of the basic factors controlling the rate of nucleation and the energy involved in the shearing process. Further work in the field of phase transformation in pure metals is obviously necessary to answer these questions.

#### Titanium-Molybdenum System

On the basis of the Hume-Rothery rules governing the formation of solid solutions, titanium and molybdenum should be completely soluble in each other at high temperature. Previous work on this system<sup>8</sup> and additional unpublished results obtained in this laboratory have confirmed this prediction. At temperatures below the  $\alpha$ - $\beta$  transformation of titanium, the solubility of molybdenum in  $\alpha$  titanium is apparently very small and the preliminary results<sup>8</sup> indicate that the Ti-Mo phase diagram below 882°C may be similar to the Fe-Ni diagram.

The results of the present study will be described in two parts, the equilibrium phase boundaries be-





71 pct Mo quenched from  
871°C ( $\alpha + \alpha'$ ).

4.35 pct Mo quenched from  
816°C ( $\alpha + \beta$ ).

10.85 pct Mo quenched from 816°C ( $\alpha + \beta$ ).

Fig. 6—Structure of Ti-Mo alloys quenched from 871° and 816°C.

tween 650° and 882°C and the effect of rate of cooling on the  $\beta$  to  $\alpha$  transformation in alloys containing less than 12 pct Mo.

**Equilibrium Boundaries Between 650° and 882°C:** A series of Ti-Mo alloys containing up to about 20 pct Mo were prepared by the arc-melting method described above. All the alloys were first heated to 980°C for 24 hr and quenched in water. Subsequently they were held at constant temperature for 5 days at 871°C and at 816°C, 10 days at 760°C, 20 days at 700°C, and 30 days at 650°C. The alloy compositions and the structures observed after heat treatment are shown by symbols on Fig. 4.

After quenching from 980°C, the alloys containing 2.3, 3.2, 4.35, 5.6, and 10.85 pct Mo had the typical Widmanstätten microstructure (cf. Fig. 5) found in titanium alloys in which the high temperature  $\beta$  solid solution is transformed, at least partially, into the supersaturated  $\alpha$  solid solution. For simplicity, this supersaturated solid solution will be called  $\alpha'$ , following the nomenclature used by Troiano and McGuire<sup>16</sup> in their study of the Fe-Mn system. The alloy containing 12.7 pct Mo, after quenching, had the  $\beta$ -retained structure (cf. Fig. 5). Hence, the minimum amount of molybdenum necessary to retain the  $\beta$  structure after quenching is around 12 pct Mo.

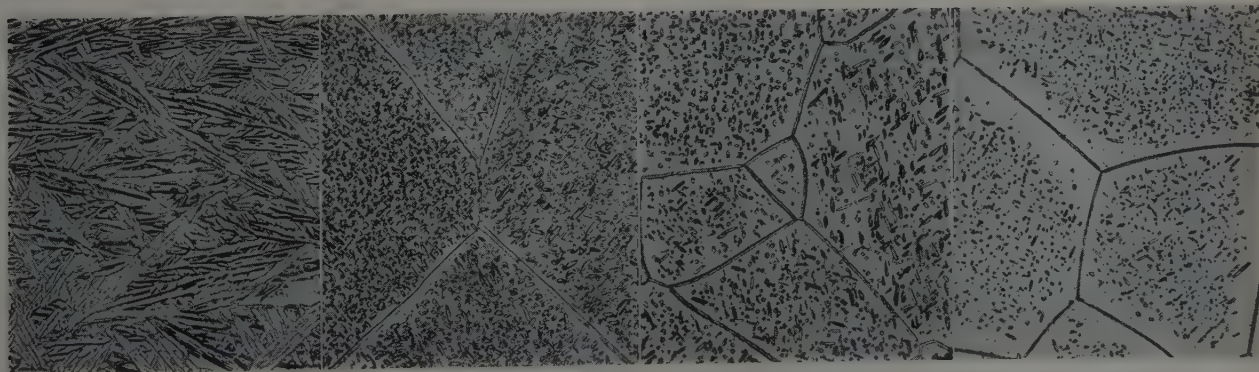
X-ray diffraction patterns were also taken of the alloys quenched from 980°C. In order to obtain the sharpest possible patterns, the powder was first filed from the quenched specimens, sealed in evacuated quartz tubes, reheated rapidly to 980°C for 5 min, and then quenched in liquid argon.<sup>†</sup> In spite of these precautions, the patterns were not sharp enough to show resolved doublets in the back-reflection range. This lack of resolution is probably

due to the strain introduced by the alloying element in a supersaturated  $\alpha$  titanium lattice.

In spite of their lack of sharpness, the X-ray diffraction patterns indicated quite clearly that, in addition to the  $\alpha'$  phase, the  $\beta$  phase was also present in alloys containing 4.35, 5.6, 9.35, and 10.85 pct Mo. Judging from the relative intensity of the  $\alpha'$  and the  $\beta$  patterns, it was also clear that the amount of the  $\beta$  phase was increasing with molybdenum content. This behavior is very similar to the well-known phenomenon of retained austenite in steels. A quantitative study of the relative amount of  $\alpha'$  and retained  $\beta$  could probably be made by using the special X-ray diffraction methods successfully applied by Averbach and Cohen<sup>17</sup> for determining the amount of retained austenite.

The structure of the alloys was investigated by microscopy after attaining equilibrium at 871°C and below. After the 871°C treatment, alloys with 4.35 and 7.1 pct Mo contained  $\alpha$  in a matrix of  $\alpha'$ , the latter formed by the transformation of  $\beta$  during cooling, as shown in Fig. 6. The alloy containing 10.85 pct Mo was  $\alpha'$  and the alloys containing 12.7 and 14.3 pct Mo had the  $\beta$ -retained structure. These results, shown by symbols on the diagram of Fig. 4, indicate that at 871°C the phase boundary between the  $\alpha + \beta$  and the  $\beta$  fields must cross the 871°C line between 7.1 and 10.87 pct Mo. This location of the phase boundary is compatible with the fact that in the alloys containing 4.35 and 7.1 pct Mo the  $\beta$  phase was not retained after quenching. In these alloys the  $\beta$  phase contains less than the critical value of 12 pct Mo and consequently transforms into  $\alpha'$  dur-

<sup>†</sup> As is explained in ref. 16, titanium powder reacts with water during quenching and a change in lattice parameter of  $\alpha$  titanium, probably due to absorption of oxygen, has been observed.



1.8 pct Mo ( $\alpha + \beta$ ).

10.85 pct Mo ( $\alpha + \beta$ ).

12.7 pct Mo ( $\alpha + \beta$ ).

14.3 pct Mo ( $\alpha + \beta$ ).

Fig. 7—Structure of Ti-Mo alloys quenched from 760°C.



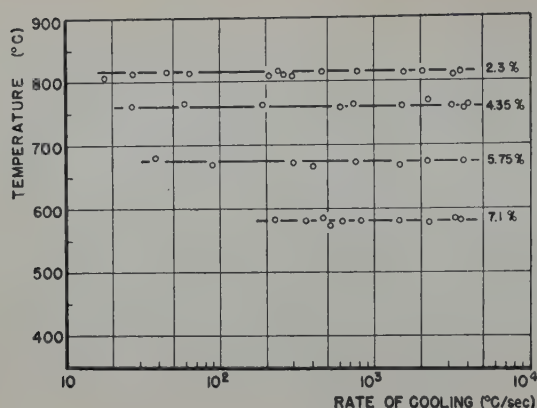


Fig. 8—Effect of the rate of cooling on the transformation temperature of Ti-Mo beta solid solution for various molybdenum concentrations.

ing quenching. The  $\alpha'$  structure in the alloy containing 10.85 pct Mo after the 871°C treatment is also logical, since this alloy was in the  $\beta$  field at temperature, but does not contain enough molybdenum to retain the  $\beta$  structure.

After the heat treatments at 816°, 760°, 700°, and 650°C, all the alloys contained either the two phases,  $\alpha$  and  $\beta$ , or the  $\beta$  phase only. These results are shown by appropriate symbols in the phase diagram of Fig. 4. Typical microstructures of some of the alloys are shown in Figs. 6 and 7. From these results, the phase boundary between the  $\alpha+\beta$  and the  $\beta$  fields may be traced as indicated in Fig. 4. It is, of course, impossible to describe the accuracy in the location of this phase boundary by means of numbers referring to either temperature or concentration. A good estimate of the accuracy can be gained by drawing the boundaries that would be shifted most towards low and high concentration and would still separate the two phase from the one phase alloy. It is believed that these two curves would not be further apart than 1 pct Mo, at the most.

No attempt was made to determine the boundary between the  $\alpha$  and the  $\alpha+\beta$  phases. The solubility of molybdenum in  $\alpha$  titanium, however, is probably very small. The alloy containing 0.8 pct Mo was found to be in a two-phase region at 700°C. A few X-ray diffraction patterns were made from other alloys containing less than 1 pct Mo and no appreciable shift in the powder pattern could be detected. It seems therefore that the solubility of molybdenum in  $\alpha$  titanium is less than 1 pct and high accuracy X-ray diffraction measurements will be necessary to establish the solubility limits.

The study of the phase diagram was not pursued at temperatures below 650°C because of the sluggishness of the reactions. It was found, for example,

that at 625°C equilibrium structures were not obtained after six weeks at temperature. The knowledge of the phase boundaries below 650°C, however, is not necessary for interpreting the results of the experiments made with high rates of cooling.

**Phase Transformation at High Rates of Cooling:** Since the alloys containing less than about 12 pct Mo transform from  $\beta$  to  $\alpha'$  during quenching, it was anticipated that the temperature at which this transformation takes place could be detected by thermal analysis. Alloys containing 2.3, 4.35, 5.75, 7.1, 8.15, 9.35, and 12.7 pct Mo were tested and temperature vs. time curves were recorded at various rates of cooling. For the alloys containing 2.3, 4.35, 5.75, and 7.1 pct Mo, a clearly defined thermal arrest was observed. Within the limits of experimental errors, the rate of cooling had no effect on the temperature at which the thermal arrest occurred (cf. Fig. 8). It is therefore established that Ti-Mo alloys containing 0 to 7.1 pct Mo transform from a  $\beta$  solid solution to a supersaturated  $\alpha$  solid solution at a temperature which is independent of the rate of cooling. This temperature decreases with increasing molybdenum content following a smooth curve, as shown in Fig. 4 (curve M).

The thermal analysis experiments made on the alloys containing 8.15, 9.35, and 12.7 pct Mo failed to reveal a thermal arrest. This is not surprising for the alloy containing 12.7 pct Mo, since in this alloy the  $\beta$  structure is retained after quenching. In the alloys containing 8.15 and 9.35 pct Mo, the results of microscopy and X-ray diffraction described in a previous section indicated that at least some of the high temperature  $\beta$  phase was transformed into supersaturated  $\alpha$  during quenching. For these alloys, the failure in measuring a heat effect by thermal analysis may be due to the fact that only a relatively small portion of  $\beta$  is undergoing the transformation and the method of measurement is not sufficiently sensitive to record a heat effect. In any case, it seems logical to assume that the partial transformation from  $\beta$  to  $\alpha'$  in the range of concentration from about 8 to about 11 pct Mo takes place at temperatures below 500°C and the transformation temperature vs. concentration curve in this range is probably an extension of the curve measured for lower concentrations. It is interesting to point out that by extrapolating the solid curve M of Fig. 4 to higher concentrations (as shown by the dotted portion of the curve), it appears that the transformation temperature would be below room temperature when the molybdenum concentration is about 12 pct. This is the approximate concentration above which the  $\beta$  phase is actually retained after quenching from high temperature.

### Allotropic Transformation in Titanium Alloys

The striking analogy between the Ti-Mo alloys and some of the Fe-base binary alloys, like those with nickel or manganese, strongly suggests that the atomic mechanisms by which the transformation takes place in the two classes of alloys are very similar, and the Ti-Mo transformation would be of the martensitic type. Obviously, the results of the present investigation do not demonstrate that all the characteristic features of a martensite reaction exist in the Ti-Mo system. However, since the reaction takes place, at least partially, at rates of cooling of the order of 10,000°C per sec, it is difficult to refute the conclusion that the reaction is diffusionless. In addition, it was shown that the temperature at

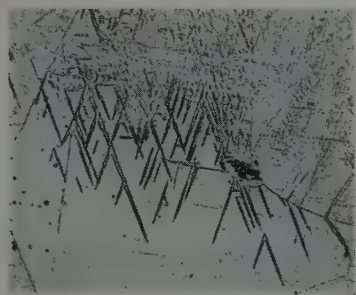


Fig. 9—Typical martensite-like structure in a Ti-Mo alloy (5 pct Mo) quenched from 980°C.



which the reaction takes place is independent of the rate of cooling. Therefore, two important characteristics of the martensite reaction have been found in Ti-Mo alloys.

It may be of interest also to point out that in some cases micrographs showing the typical structure of martensite needles have been obtained. Fig. 9 shows a Ti-Mo alloy containing 9.5 pct Mo prepared with titanium powder obtained from the Bureau of Mines and quenched from the  $\beta$  field.<sup>†</sup> The rather large  $\alpha'$  needles in a  $\beta$  matrix are very similar to martensite in austenite. The occurrence of well-defined isolated needles, as shown in Fig. 9, was rather rare in the specimens studied in the present investigation, probably because too large a portion of the  $\beta$  phase was transformed. There is probably a critical and narrow range of molybdenum concentration for which only a small fraction of the  $\beta$  phase would be transformed by quenching to room temperature, and in this range more typical martensitic needles could likely be obtained.

The thermal analysis method used in this investigation is not suitable for a complete study of the finer details involved in a martensite reaction. It is probable that there is a temperature interval between the beginning and the end of the reaction. By thermal analysis, it is possible to detect only the temperature at which the bulk of the heat is released. This temperature probably corresponds to that which is sometimes referred to as the burst temperature for the martensite reaction.

Finally, the atomic mechanism of the transformation in titanium alloys of the Ti-Mo type remains unknown. The only clue to a possible mechanism is the work of Burgers on the crystallographic relationships in the transformation of pure zirconium.<sup>18</sup>

### Conclusions

1—The temperature at which titanium transforms from the  $\beta$  form (body-centered cubic) to the room temperature  $\alpha$  form (hexagonal close-packed) decreases progressively from 882°C to about 850°C with increasing rate of cooling from 4° to 10,000°C per sec. A similar effect has been found for zirconium, for which the drop in temperature is from 865° to 850°C. The transformation temperature of thallium (also from body-centered cubic to hexagonal close-packed) is not affected by rates of cooling up to 8000°C per sec. The body-centered cubic to hexagonal close-packed transformation in these three metals is therefore a diffusionless transformation and is probably the result of a combination of shear and homogeneous change in volume.

2—The solid state phase boundaries in the Ti-Mo system have been established above 650°C. Alloys quenched from the  $\beta$  field transformed into an  $\alpha$  supersaturated solid solution (called  $\alpha'$ ) for molybdenum concentration up to about 12 pct. The transformation is only partial from about 4 to 12 pct Mo. Above 12 pct Mo, the  $\beta$  structure is retained.

3—From 0 to 8 pct Mo, the temperature at which  $\beta$  transforms entirely or partially to  $\alpha'$  was measured by thermal analysis. This temperature is not affected by the rate of cooling. For molybdenum concentration between 8 and 12 pct, no heat effect was detected during cooling although it was found by both X-ray diffraction and microscopy that  $\alpha'$  was present

after quenching. The heat released in the case of partial transformation was probably too small to be detected by thermal analysis.

4—The analogy between the Ti-Mo alloys and some binary Fe-base alloys (such as iron with nickel or manganese) suggests that the transformation in the Ti-Mo system is of the martensite type. The same type of transformation has been found in the Ti-Cr system and probably exists in other binary alloys for which there is an extensive solid solubility in  $\beta$  titanium.

### Acknowledgment

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# Crystal Structure of $\text{Ti}_5\text{Si}_3$ , $\text{Ti}_5\text{Ge}_3$ , and $\text{Ti}_5\text{Sn}_3$

by Paul Pietrokovsky and Pol Duwez

The crystal structure of the compound  $\text{Ti}_5\text{Ge}_3$  has been determined from X-ray powder diffraction data. Related silicon and tin compounds have been found to be isomorphous. Unit cell dimensions, axial ratios, and parameters for equivalent atomic positions are given.

THERE is, at present, only meager information pertaining to the solid state reactions of titanium with the elements in group 4B of the periodic table (silicon, germanium, tin, and lead). The only two compounds whose crystal structure has been established are  $\text{TiSi}_2$  and  $\text{TiGe}_2$  (references 1 and 2 respectively). These two compounds are isomorphous and have an orthorhombic symmetry  $D_{2h}^{28} - Fddd$ . The titanium-rich regions of the constitution diagrams of titanium-silicon, titanium-tin, and titanium-lead have been investigated by Craighead et al.<sup>3</sup> While valuable information concerning the alpha solid solubility of these three elements in titanium was obtained, no light was shed on the existence or nature of the titanium-rich compound in these systems. The present study is concerned with the crystal structure of the intermediate phases  $\text{Ti}_5\text{Si}_3$ ,  $\text{Ti}_5\text{Ge}_3$ , and  $\text{Ti}_5\text{Sn}_3$ , which were found to be isostructural.

The alloys were prepared by mixing the pure metal powders in the desired proportions, pressing the mixture into pellets, and melting them in an electric arc furnace in the presence of a helium atmosphere.<sup>4</sup> After melting, the specimens, weighing approximately 5 g, were sealed in evacuated quartz vials, homogenized at 1038°C for three days, and quenched from that temperature. Powder diffraction patterns were made with a 143.2 mm diam Debye-Scherrer X-ray camera in which the Ievins and Straumanis film arrangement was utilized. Filtered copper radiation was used throughout the entire investigation.

A study of the powder patterns of a series of alloys of various compositions indicated the presence of a compound around a composition corresponding approximately to a ratio of 3 titanium to 2 silicon, germanium, or tin. From a visual examination of the diffraction patterns, it was evident that the silicon and germanium alloys were iso-

morphous. For small angle reflections, the powder pattern of the tin compound was analogous to that of the silicon and germanium compounds, but after the first ten reflections, the similarity was no longer clear. The powder pattern of the germanium compound was selected for indexing, since it exhibited a weak small angle reflection and clearly resolved doublets in the back-reflection range. Good agreement between observed and calculated values of  $(1/d)^2$  was found by indexing the pattern on the basis of hexagonal symmetry. For the hexagonal system:

Table 1. Debye-Scherrer Powder Diffraction Data for  $\text{Ti}_5\text{Ge}_3$ .  
Filtered Copper Radiation.

| hkl  | d<br>Obs.<br>(Å) | (1/d) <sup>2</sup><br>Obs.<br>(Å <sup>-2</sup> ) | (1/d) <sup>2</sup><br>Calc.<br>(Å <sup>-2</sup> ) | In-<br>tensity,<br>Obs. | Relative<br>Intensity,<br>Calc. |
|------|------------------|--------------------------------------------------|---------------------------------------------------|-------------------------|---------------------------------|
| 10.0 | 6.5              | 0.0236                                           | 0.0235                                            | w                       | A*                              |
| 10.1 | —                | —                                                | —                                                 | —                       | 0                               |
| 11.0 | 3.79             | 0.0697                                           | 0.0705                                            | w                       | 29                              |
| 20.0 | —                | —                                                | —                                                 | —                       | 13                              |
| 11.1 | 3.07             | 0.1064                                           | 0.1072                                            | m                       | 175                             |
| 20.1 | —                | —                                                | —                                                 | —                       | 0                               |
| 00.2 | 2.61             | 0.1473                                           | 0.1465                                            | ms                      | 270                             |
| 21.0 | 2.47             | 0.1632                                           | 0.1645                                            | ms                      | 250                             |
| 10.2 | 2.42             | 0.1700                                           | 0.1703                                            | wm                      | 201                             |
| 21.1 | 2.22             | 0.2022                                           | 0.2012                                            | vs                      | 1000                            |
| 30.0 | 2.17             | 0.2115                                           | 0.2115                                            | ms                      | 302                             |
| 11.2 | 2.14             | 0.2175                                           | 0.2173                                            | s                       | 546                             |
| 20.2 | 2.03             | 0.2417                                           | 0.2408                                            | m                       | 125                             |
| 22.0 | —                | —                                                | —                                                 | —                       | 3                               |
| 31.0 | 1.81             | 0.3041                                           | 0.3055                                            | w                       | 78                              |
| 21.2 | —                | —                                                | —                                                 | —                       | 8                               |
| 22.1 | 1.77             | 0.3179                                           | 0.3187                                            | m                       | 118                             |
| 00.3 | —                | —                                                | —                                                 | —                       | 0                               |
| 31.1 | 1.71             | 0.3406                                           | 0.3422                                            | s                       | 321                             |
| 10.3 | —                | —                                                | —                                                 | —                       | 0                               |
| 30.2 | 1.67             | 0.3572                                           | 0.3583                                            | w                       | 13                              |
| 40.0 | —                | —                                                | —                                                 | —                       | 3                               |
| 11.3 | 1.58             | 0.3990                                           | 0.4008                                            | w                       | 21                              |
| 20.3 | —                | —                                                | —                                                 | —                       | 0                               |
| 22.2 | 1.52             | 0.4311                                           | 0.4288                                            | m                       | 85                              |
| 32.0 | —                | —                                                | —                                                 | —                       | 5                               |
| 31.2 | —                | —                                                | —                                                 | —                       | 3                               |
| 32.1 | 1.441            | 0.4817                                           | 0.4823                                            | w                       | 6                               |
| 41.0 | 1.422            | 0.4946                                           | 0.4935                                            | s                       | 42                              |
| 21.3 | 1.422            | 0.4946                                           | 0.4948                                            | s                       | 209                             |
| 40.2 | 1.383            | 0.5229                                           | 0.5228                                            | m                       | 39                              |
| 50.0 | 1.306            | 0.5867                                           | 0.5875                                            | —                       | 198                             |
| 00.4 | 1.306            | 0.5867                                           | 0.5872                                            | s <sub>b</sub> **       | 66                              |
| 32.2 | 1.301            | 0.5911                                           | 0.5933                                            | m                       | 66                              |
| 22.3 | 1.278            | 0.6126                                           | 0.6123                                            | wm                      | 42                              |
| ***  | —                | —                                                | —                                                 | —                       | —                               |

\* Calculated intensity not significant because of absorption.

\*\* A broad strong reflection due to overlapping.

\*\*\* Thirty-five additional reflections with spacing smaller than 1.27 Å were observed.

vs = very strong, s = strong, ms = medium strong, m = medium, wm = weak medium, w = weak.

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$$(1/d)^2 = A(h^2 + hk + k^2) + B(1)^2 \quad [1]$$

$$A = \frac{4}{3a^2}, \quad B = \frac{1}{c^2}$$

The results of these computations are shown in Table I.

A similar method of indexing was applied to the titanium-silicon and titanium-tin compounds, and in all cases, good agreement was obtained between calculated and observed interplanar spacings. The values of the constants  $A$  and  $B$  in the quadratic eq 1 and the lattice parameters of the three compounds are given in Table II. The parameters were ob-

Table II. Unit Cell Parameters for  $Ti_5Si_3$ ,  $Ti_5Ge_3$ , and  $Ti_5Sn_3$ . Parameters are expressed in Å.

| Compound   | A      | B      | $a_0$             | $c_0$             | $c_0/a_0$ |
|------------|--------|--------|-------------------|-------------------|-----------|
| $Ti_5Si_3$ | 0.0239 | 0.0375 | $7.465 \pm 0.002$ | $5.162 \pm 0.002$ | 0.692     |
| $Ti_5Ge_3$ | 0.0235 | 0.0367 | $7.537 \pm 0.002$ | $5.223 \pm 0.002$ | 0.693     |
| $Ti_5Sn_3$ | 0.0258 | 0.0336 | $8.049 \pm 0.002$ | $5.454 \pm 0.002$ | 0.678     |

tained by applying the least squares method to the large angle reflections.

An attempt to elucidate the structure of the titanium-germanium compound was made on the basis of the powder pattern. The only systematic extinctions in the Debye-Scherrer patterns are those of the  $(h0l)$  reflections for  $l \pm 2n$ . This indicates the presence of a mirror glide plane with a displacement  $c/2$  parallel to the  $c$  axis. Since no other systematic extinctions were observed, five space groups are possible, namely  $D_{3d}^4$ ,  $C_{3v}^{18}$ ,  $D_{6h}^8$ ,  $C_{6v}^{18}$ , and  $D_{3h}^6$ . Since a further reduction in the number of likely space groups is not possible from the powder data, it was decided to initiate a survey of the literature prior to finding the Laue symmetry. This survey failed to uncover any similitude with a compound of the  $A_3B_2$  type, but an analogy was found with  $Mn_5Si_3$ . The structure of  $Mn_5Si_3$ , determined by Åmark, Borén, and Westgren,<sup>5</sup> is hexagonal and belongs to the space group  $D_{3h}^6 - C 6/mcm$  (type  $D8_3$ ). The unit cell contains 16 atoms in the following positions.\*

4 Mn I in  $(d)$ :  $1/3 \ 2/3 \ 0$ ;  $2/3 \ 1/3 \ 0$ ;  $1/3 \ 2/3 \ 1/2$ ;  $2/3 \ 1/3 \ 1/2$ .

6 Mn II in  $(g)$ :  $x0\frac{1}{4}$ ;  $0x\frac{1}{4}$ ;  $\bar{x}\bar{x}\frac{1}{4}$ ;  $\bar{x}0\frac{3}{4}$ ;  $0x\frac{3}{4}$ ;  $xx\frac{3}{4}$ .

$x = 0.23$ .

6 Si in  $(g)$ :  $x = 0.60$ .

A perspective drawing of the structure is shown in Fig. 1.

Assuming this structure to be the correct one for the titanium-germanium compound, intensity computations were made using the well-known formula:

$$I = \text{constant} [F(hkl)]^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

In view of the large number of reflections present (57 for  $Ti_5Ge_3$ ), no correction for absorption was included in the calculated intensities. Only the first reflection (100) suffers greatly from this oversight. With the exception of the (100) reflection, the agreement between calculated and observed intensities (Table II) is quite satisfactory. Similar com-

\* An error in the tabulation of nearest neighbors to the silicon atom in the position  $[\bar{x}\bar{x}\frac{1}{4}]$ ,  $x = 0.60$ , should be corrected in ref. 6. The atom designated  $f'$  and the two atoms marked  $f''$  are Mn II atoms and not Si atoms; the number of nearest neighbors to the silicon atoms having the structural symmetry  $C 2v - mm$  are 4 Mn I atoms, 3 Mn II atoms, and 6 Si atoms.

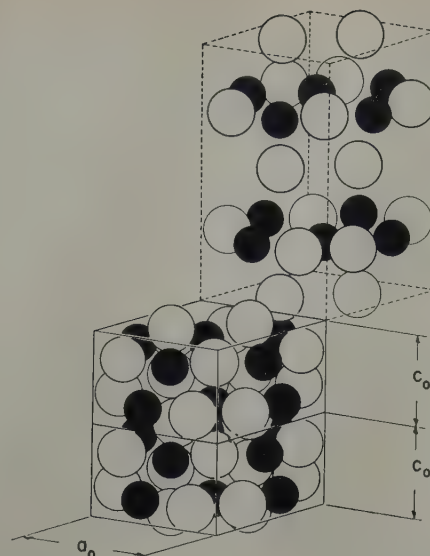


Fig. 1—Perspective drawing of two cells of  $Ti_5(Si, Ge, Sn)_3$  (lower left) and of one cell expanded in the  $c$  axis direction (upper right).

putations were made for  $Ti_5Si_3$  and  $Ti_5Sn_3$ , and in all cases, the observed intensities were in good agreement with the calculated values.

From the point of view of a systemization of the structure of intermetallic compounds between the transition elements of the first series and the elements of the 4B group of the periodic table, it is interesting to note that the only other intermetallic compound reported so far as being isomorphous with  $Mn_5Si_3$  is the  $\eta$  phase ( $Fe_5Si_3$ ) in the iron-silicon system.<sup>7,8</sup> It is probable that other compounds of the  $Mn_5Si_3$  type exist between the transition elements and silicon, germanium, and tin.

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# Role of Gases in the Production of High Density Powder Compacts

by Donald Warren and J. F. Libsch

THIS investigation originated as a result of a previous experimental study<sup>1</sup> of the magnetic properties of Fe-Co alloys fabricated by the powder metallurgy technique. Densities of powder compacts prepared for the magnetics investigation varied from 7.45 to 7.70 g per cu cm or from 93 to 95 pct of the experimental value of 8.08 g per cu cm for a fused alloy of the same composition.<sup>2</sup> While this range of density is considered sufficiently high for most applications, the highest possible density is to be desired for maximum magnetic properties.

By applying a technique similar to the one described above to a pure electrolytic iron powder, Rostoker<sup>3</sup> was able to achieve a density of 7.895 g per cu cm, which is the highest density ever reported for sintered iron. While Rostoker's work involved the sintering of an elemental powder rather than a mixture, it was believed that higher densities should also have been obtained for alloys using the above technique because of the recoining operation and the high sintering temperature. Consequently, it was decided to investigate the various factors affecting the density of this alloy with the idea that such a study might lead to higher densities and, as a result, powder alloys having magnetic properties identical with those of the fused alloys.

It was believed that the principal reason that near-theoretical densities for the powdered alloy were not obtained was the interference of gases with the normal sintering mechanism. When present during the sintering operation, gases can exert several harmful effects: they can remain on the particle surface and interfere with surface diffusion and plastic flow; they can be released and, under certain conditions, expand the void spaces through gas pressure; or they can remain trapped in the pores and exert a hydrostatic pressure that retards elimination of the pores.

Jones,<sup>4</sup> Rhines,<sup>5</sup> Goetzel,<sup>6</sup> and others have given the effect of gases in the sintering of powder compacts an extensive treatment. Among the more important sources of gases in the sintering process are dissolved gases, adsorbed gases, air entrapped during pressing, and gaseous products of chemical reactions. During sintering adsorbed gases are partly released at a relatively low temperature, while those gases entrapped during pressing cannot escape until their pressure is increased sufficiently through increasing temperature to expand the interparticle openings. The remaining adsorbed gases, gaseous reduction products, and dissolved gases produce a similar effect at the higher temperatures. If, in the

sintering process, gas evolution occurs after the inter pore channels have been sealed, an exaggerated expansion of the void spaces results. This is particularly true if the temperature is high enough for extensive plastic flow.

In his fabrication of powder bars from tantalum, Balke<sup>7</sup> had to consider the effect of adsorbed hydrogen and provide for its escape during sintering by limiting the compacting pressure to a maximum of 50 tons per sq in. The effect of gases entrapped during pressing was first noted by Trzebiatowski<sup>8</sup> when he found that gold and silver powders decrease in density with increasing sintering temperature if pressed at 200 tsi, while they exhibit the usual increase when pressed at 40 tsi. Recent investigators<sup>9-11</sup> have also noted that entrapped gases have an effect on the expansion of copper compacts during sintering. Proper provision for the escape of gaseous products of reduction must be made in order to avoid deleterious effects. Myers<sup>12</sup> states that in the sintering of electrolytic tantalum powder, the temperature was gradually raised to 2600°F with a pause at 2000°F to permit reduction of the oxides.

## Experimental Details

For the present study, 50 pct Co-50 pct Fe compacts in the form of circular disks 1½ in. in diam and 0.15 in. thick were fabricated by the pressing and sintering of a mixture of the elemental powders. It was decided to follow the sintering process by means of liquid permeability measurements, because it was thought that such measurements might serve as a measure of relative pore sizes, as well as a possible indication of the point at which most of the inter pore channels become sealed. However, since the permeability as measured by the flow of a liquid, such as ethylene glycol, does not give an absolute indication of the point where the pores have become isolated, a method for determining the percentage of pores connected to the surface was set up. As an additional cross check on the permeability measurements, metallographic methods were used to study the relative pore size. Finally, the property of ultimate interest, the density, was measured.

**Raw Materials:** The powders used consisted of an annealed, 99.9 pct pure, -150 mesh grade of electrolytic iron powder, and a 98 pct pure, -200 mesh grade of reduced and comminuted cobalt powder. The cobalt powder was not further processed either by hydrogen reduction or annealing.

The screen analyses for the iron and cobalt powders are given in Table I, while the chemical analyses for each type of powder are listed in Table II. Table III gives the hydrogen loss measurements for the powders according to the M.P.A. Standard Method and for a higher temperature as well.

**Preparation of Compacts:** Equal amounts of the elemental powders were mixed by rotation for 1 hr and then pressed into compacts approximately 0.15

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Table I. Screen Analyses of Powders

| Size Range | Fe Powder, Pct | Co Powder, Pct |
|------------|----------------|----------------|
| +80 mesh   | Trace          | Trace          |
| -80 +100   | Trace          | Trace          |
| -100 +150  | Trace          | Trace          |
| -150 +200  | 8.75           | Trace          |
| -200 +325  | 22.80          | 0.96           |
| -325       | 68.40          | 99.00          |

in. thick in a single acting die lubricated with a 3 pct stearic acid solution. The equipment used for pressing and sintering the compacts has been described previously.<sup>8</sup> It should be mentioned that the compacts, except where otherwise stated, were placed in the furnace directly at the sintering temperature and required about 5 to 10 min to reach temperature.

**Permeability Measurements:** The permeability of the compacts was measured by a method similar to the one devised by Chadwick and Broadfield.<sup>18</sup> The apparatus consisted of a Witt filter flask in which was mounted a filter funnel feeding into a graduated cylinder inside the flask. When the flask was evacuated with a Cenco Hy-Vac pump, the atmospheric pressure caused the compact to seat itself against a thin rubber sleeve placed in the filter funnel and thus provide an air-tight connection. Ethylene glycol was used as the permeating medium because of its low viscosity and vapor pressure and lack of corrosive action. The time required for 5 ml of glycol at a temperature of 30°C to pass through a compact of approximately 0.15 in. thickness under a pressure difference of more than 75 cm of mercury was measured. In some instances where the permeability was very low and the times required were very long, the measurement was limited to only 2 or 3 ml of flow. In all cases, the permeability was reported as ml per in.<sup>2</sup> min where in.<sup>2</sup> refers to the surface area of the compact.

**Pore Volume and Density Measurements:** After a compact had been given its final fabricating treatment, it was cleaned in acetone, oven-dried, and weighed on an analytical balance. The compact was then immersed in xylene and a vacuum pulled on it to remove the air from the pores and allow the xylene to enter. The weight of the compact in xylene, maintained at a temperature of 30°C ±1°C, was then measured. After being oven-heated to drive off the xylene, the compact was given several applications of Dekadhesse to provide a thin coating that was impervious to water. Next, the coating was oven-baked, and finally, the weight of the compact in air and in water was determined. Those compacts which had densities equal to 95 pct or more of the theoretical density were not coated with Dekadhesse but were weighed directly in water.

The following is an outline of the method used for calculating pore volume and density from the measurements described above:

$$\text{Bulk volume of the compact} = \frac{W_{CA} - W_{CW}}{D_W} \quad [1]$$

Table II. Chemical Analyses of Powders

|           | C, Pct | Mn, Pct | Si, Pct | Cu, Pct | Ni, Pct |
|-----------|--------|---------|---------|---------|---------|
| Fe powder | 0.048  | 0.04    |         |         |         |
| Co powder | 0.069  | 0.11    | 0.13    | 0.075   | 0.5     |

where  $W_{CA}$  is the weight of compact in air after coating with Dekadhesse;  $W_{CW}$ , the weight of compact in water after coating with Dekadhesse; and  $D_W$ , the density of water at temperature of measurement.

$$\text{Subsurface volume of the compact (volume of the metal itself plus isolated pores)} = \frac{W_A - W_x}{D_x} \quad [2]$$

where  $W_A$  is the weight of compact in air;  $W_x$ , the weight of compact in xylene; and  $D_x$ , the density of

Table III. Hydrogen Loss Measurements

|                          | Fe Powder, Pct | Co Powder, Pct |
|--------------------------|----------------|----------------|
| 1 hr at 1050°C           |                |                |
| (Standard M.P.A. Method) | 0.4            | 1.3            |
| 30 min at 1400°C         | 0.4            | 1.4            |
| 1 hr at 1400°C           | 0.4            | 1.4            |

xylene at temperature of measurement (for these experiments  $D_x = 0.855$  g per cu cm at 30°C).

$$\text{Volume of surface connected pores} = \frac{W_{CA} - W_{CW}}{D_W} - \frac{W_A - W_x}{D_x} \quad [3]$$

$$\text{Volume of metal alone} = \frac{W_A}{8.08} \quad [4]$$

where 8.08 g per cu cm is the density of the fused 50 pct Fe-50 pct Co alloy.<sup>2</sup>

$$\text{Total volume of the pores} = \frac{W_{CA} - W_{CW}}{D_W} - \frac{W_A}{8.08} \quad [5]$$

$$\text{Density of the compact} = W_A \div \frac{W_{CA} - W_{CW}}{D_W} \quad [6]$$

The densities of those compacts which had to be coated with Dekadhesse before weighing in water are accurate only to about 0.01 g per cu cm because of the error introduced by the coating. However, for those compacts having a density equal to or greater than 95 pct of the theoretical density, the density is correct to 0.001 g per cu cm.

In the experimental results the volume of the surface connected pores is expressed as a percentage of the total pore volume. The accuracy of this value depends upon the error introduced by the Dekadhesse coating in the bulk volume measurement and as such it varies with the total amount of porosity. Where the total porosity is high, the percentage of surface connected pores is correct to ±1 pct and where the total porosity is low, this value is correct only to ±5 pct.

**Metallographic Examination:** The samples for metallographic examination were first impregnated with a very thin varnish and oven-baked. After being ground and polished, the compacts were electrolytically etched in a 10 pct nitric acid solution in order to remove the flowed metal covering the pores and then etched for 2 to 3 min by immersion in a 4 pct picral solution to reveal the grain boundaries.

### Experimental Observations on Compacting and Sintering Procedures

**Effect of Compacting Pressure:** The effect of compacting pressure upon the permeability, density, and percentage of pores connected to the surface of green compacts is shown in Fig. 1.

The fact that practically 100 pct of the pores are connected to the surface in specimens compacted at

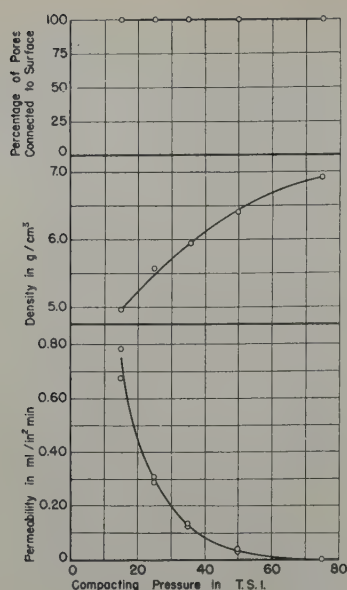


Fig. 1—Effect of compacting pressure.

pressures up to 75 tsi indicates that there is little likelihood of entrapped gases in these compacts. This is in accordance with the views of Kamm, Steinberg, and Wulff,<sup>9</sup> who feel that there is very little possibility of entrapping gases during the pressing of relatively hard powders, such as iron and nickel.

Figs. 2 and 3 are micrographs of compacts pressed at 25 and 75 tsi, respectively. (It was necessary to sinter these compacts at 800°C for metallographic preparation.) The larger particles of iron are most prominent, while the lighter areas consist of the finer particles of iron and cobalt which have already begun to sinter.

*Effect of Sintering Time and Temperature upon Compacts Pressed at 25 tsi:* The results of these experiments are summarized in Figs. 4 and 5. It is important to stress the fact that none of the increases in permeability would be predicted if the sintering process were being followed by means of density measurements alone, as can be seen from the lower set of curves in Fig. 5. The only irregularity observed in the density vs. sintering time curves is that the entire curve for 1000°C lies below that for 800°C. This apparent anomaly has been noted by other investigators<sup>11, 14</sup> and has been attributed to various factors connected with the  $\alpha$  to  $\gamma$  phase transformation.

While a study of the density values gives no

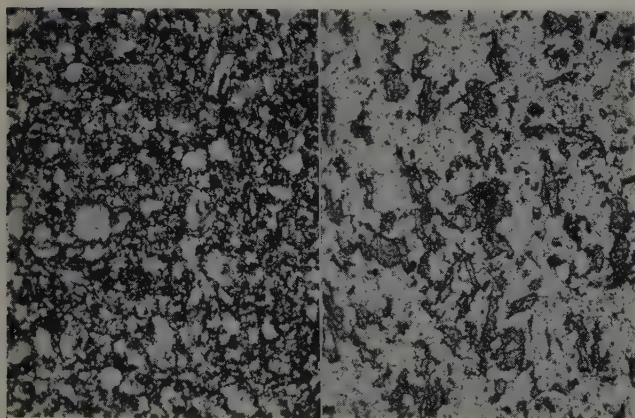


Fig. 2—Pressed at 25 tsi, sintered 15 min at 800°C. X100.

Fig. 3—Pressed at 75 tsi, sintered 15 min at 800°C. X100.

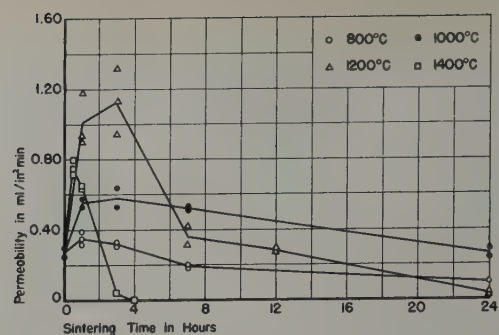


Fig. 4—Effect of sintering time and temperature upon the permeability of compacts pressed at 25 tsi.

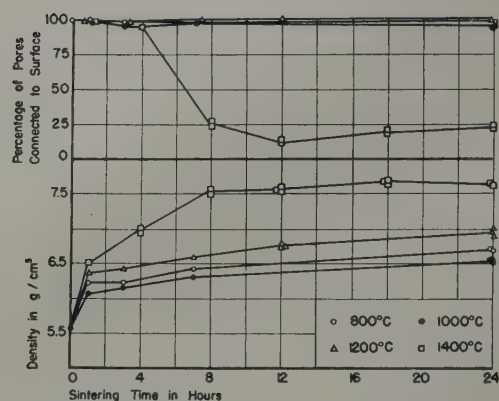


Fig. 5—Effect of sintering time and temperature upon the density and pore volume of compacts pressed at 25 tsi.

reason for the increases observed in the permeability values, metallographic examination does. Figs. 6, 7, 8, and 9 are micrographs of compacts sintered 1 hr at 800°, 1000°, 1200°, and 1400°C, respectively. It can be seen that the individual pores become increasingly well-defined with increasing sintering temperature, and that those pores in the compact sintered at 1400°C have been blown up tremendously. Metallographic examination showed that the microstructure of the compact sintered 3 hr at 1200°C was essentially the same as that of Fig. 8.

Since the individual pores have been expanded to a greater extent after an hour sinter at 1400°C than after a similar sinter at 1200°C, it might be expected that the permeability values for the former will be greater than those for the latter. But such is not the case. In order to resolve the apparent disagreement, it should be remembered that the resistance of a powder compact to liquid flow in a permeability measurement depends not only upon the pore size but also upon the degree to which the pores are interconnected. It is here that a metallographic study fails to tell the complete story. It would be expected that at 1400°C, the interpore channels would be sealed more rapidly than at 1200°C. This is borne out by the following observations: 1—the greater expansion of individual pores at 1400°C, which requires the prior sealing of interpore channels; 2—the absence in Fig. 9 of the network of fine pores present in Fig. 8; and 3—the large decrease in percentage of pores connected to the surface for compacts sintered more than 4 hr at 1400°C, Fig. 5. From the above discussion, it can be seen that the permeability value for a powder compact depends upon the balance between the shrinkage produced by normal sintering and the expansion due to the presence of evolved gases.



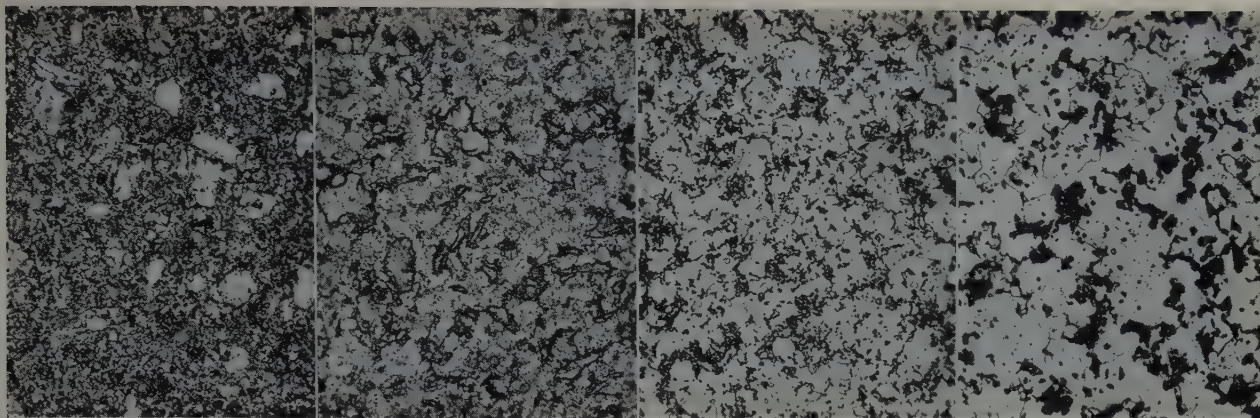


Fig. 6—Pressed at 25 tsi, sintered 1 hr at 800°C. X100.

Fig. 7—Pressed at 25 tsi, sintered 1 hr at 1000°C. X100.

Fig. 8—Pressed at 25 tsi, sintered 1 hr at 1200°C. X100.

Fig. 9—Pressed at 25 tsi, sintered 1 hr at 1400°C. X100.

Of the sources of gases in the sintering process, it is believed that chemisorbed gases and gaseous reduction products are primarily responsible for the pore expansion observed in compacts sintered at 1200° and 1400°C. Some idea of the oxide content of the cobalt and iron powders can be obtained from the hydrogen loss values given in Table III. The existence of such oxides, either as surface films or inclusions in the powder, is detrimental because the reduction of oxides by hydrogen used as a sintering atmosphere or by carbon in the powders themselves (see Table II) will lead to the evolution of gases. The detrimental effect of oxides has been shown by Cordiano,<sup>15</sup> who obtained a decrease in density with increase in hydrogen loss for iron compacts sintered for short times. The reduction of cobalt and iron oxide by hydrogen begins below 500°C and is rapid at 700° to 1100°C. The fact that reduction occurs at these higher temperatures means that oxides probably contribute more to pore expansion than any other source of gases, because their gaseous reduction products must make their escape after considerable sintering (sealing of the inter pore channels) has occurred.

There is no data to show the amount of chemisorbed gases present in the powders used for this study. However, Taylor and Burns<sup>16</sup> have studied the adsorption of gases by iron and cobalt powders. Their data indicate that appreciable quantities of CO and CO<sub>2</sub> were adsorbed by cobalt powder, while only small quantities were adsorbed by iron powder. It was also indicated that there was considerably more adsorption by a partially oxidized lot of cobalt powder than by a completely reduced lot of the same powder. Since their adsorption values decrease with increasing temperature, it is reasonable to expect that in the heating of a green compact, the bulk of adsorbed gases would be driven off before appreciable sintering could occur. Whether or not the escape of such gases expands the pores depends upon the degree of powder compaction and the heating rate during sintering. In the case of the present experiments, the compacts were placed in the furnace at the sintering temperature and required only 5 to 10 min to reach that temperature. With such a high heating rate, the presence of adsorbed gases becomes significant.

*Effect of Sintering at 1400°C upon Compacts Pressed at 25, 50, and 75 tsi:* The results of these experiments are presented in Fig. 10. A study of this figure shows that for the first time, the pore expansion (as indicated by an increase in permeability)

could be detected by a decrease in density. However, this was true only of the density curve for a pressure of 75 tsi. It is important to note that the density values after a 24 hr sinter at 1400°C decrease in order of increasing compacting pressure, which is just the opposite of what might be expected.

That the early increases in the permeabilities are caused by expansion of the pores is borne out by Figs. 11 and 12, which present a clear picture of the relative pore sizes in compacts pressed at 25 and 50 tsi, respectively, and then sintered for 30 min at 1400°C. The microstructure of the compact pressed at 75 tsi and sintered 30 min at 1400°C was similar to that of Fig. 12. Because the compacts pressed at 25 tsi were more porous in the green condition than the compacts pressed at 50 and 75 tsi, the individual pores have not been blown up to as great an extent in these as in the denser compacts.

The lesser degree of pore expansion in compacts pressed at 25 tsi is reflected in Fig. 10 by the more rapid decrease in permeability and in the percentage of pores connected to the surface between 1 and 2½ hr at 1400°C for compacts pressed at 25 tsi.

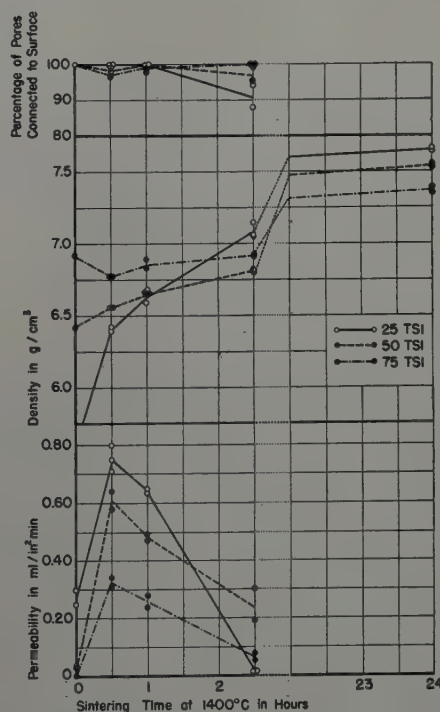


Fig. 10—Effect of sintering at 1400°C on compacts pressed at 25, 50 and 75 tsi.



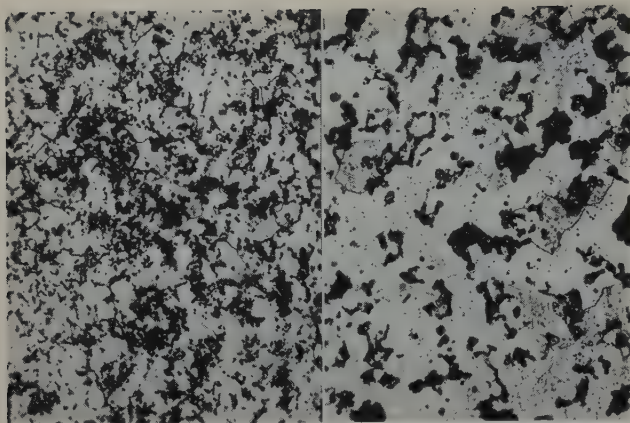


Fig. 11—Pressed at 25 tsi, sintered 30 min at 1400°C. X100.

Fig. 12—Pressed at 50 tsi, sintered 30 min at 1400°C. X100.

The lesser expansion of individual pores that occurs with the lower compacting pressures can be attributed to two factors: 1—the hydrogen has greater access to the surfaces of loosely compacted powder particles, and 2—the slower initial rate of sintering provides a greater opportunity for the oxides to be reduced and for the gaseous reduction products to escape. In the highly compressed compacts, sealing of the interpore channels begins earlier and takes place more rapidly. In such a case, the relatively small hydrogen atoms can easily diffuse into the interior of the compact, but the larger molecules of water formed by the reduction cannot diffuse outward through the lattice interstices. Thus, they must remain in the sealed off pores to either produce an actual expansion or to retard sintering.

The decrease in final density that occurs with an increase in compacting pressure for compacts sintered 24 hr at 1400°C is a reflection of the larger degree of pore expansion with the higher compacting pressures, because these larger pores are closed up at a very slow rate. Also, there is a greater possibility with the higher compacting pressures of gases being sealed off in the pores and thus retarding the later phases of sintering. Both Shaler<sup>17</sup> and Mackenzie and Shuttleworth<sup>18</sup> have given the effect of gases trapped within the pores of powder compacts an extensive mathematical treatment.

### Study of the Gases Evolved During Sintering

In the second phase of this investigation, an effort was made to relate the effects observed in the orig-

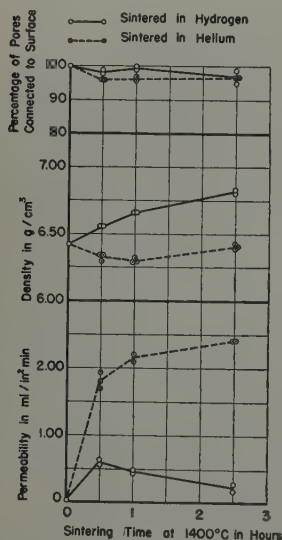


Fig. 13—Effect of sintering at 1400°C in hydrogen and helium on compacts pressed at 50 tsi.

inal experimental results with the evolution of gases and to determine, if possible, the nature of these gases.

**Effect of Sintering at 1400°C in Hydrogen and Helium on Compacts Pressed at 50 tsi:** Since it was believed that gases resulting from the reduction of oxides in or on the powder particles by the hydrogen of the sintering atmosphere was primarily responsible for the expansion of the pores, a series of compacts was pressed at 50 tsi and sintered at 1400°C in a helium atmosphere for comparison with the previous series of compacts pressed at 50 tsi and sintered at 1400°C in hydrogen. The results of this experiment are shown in Fig. 13.

The large increase in the permeability, as well as the significant decrease in the density, of a compact sintered at 1400°C in helium suggests the occurrence of a severe expansion of the individual pores leading to an overall growth in the size of the compact. That such is actually the case is shown by the microstructure of a compact pressed at 50 tsi and sintered for 30 min at 1400°C in helium, see Fig. 14.

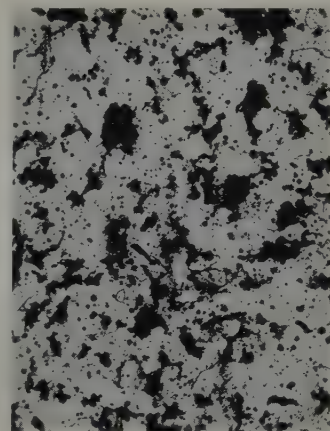


Fig. 14—Pressed at 50 tsi, sintered 30 min at 1400°C in helium. X100.

This experiment tends to relegate the effect of chemisorbed gases to a relatively minor role as far as pore expansion is concerned, because if chemisorbed gases, alone, were responsible for the effects observed, then there seems to be no obvious reason why the properties of compacts sintered in hydrogen and helium would not be fairly similar. The most logical explanation for the results observed for compacts sintered in helium seems to be that the gases were produced either by the reduction of oxide films by carbon in the powders or by thermal decomposition of the oxides.

Reduction of the oxides by carbon would probably be slower than reduction by hydrogen, because the diffusion of carbon is necessary for appreciable reduction to occur, whereas hydrogen can readily permeate the pores of the compact. According to the available data,<sup>19</sup> the only oxide of either cobalt or iron that decomposes at 1400°C or below is cobaltic oxide ( $\text{Co}_2\text{O}_3$ ) which decomposes at 895°C. Such a thermal decomposition would therefore occur at a temperature higher than that required for reduction by hydrogen. Thus, either of the two proposed mechanisms would lead to the evolution of gases at a later stage in the sintering process than if the same gases had been liberated by reduction of the oxides by hydrogen. This evolution of gases after appreciable sintering (sealing of interpore channels) had already occurred seems to account for the greater expansion of pores observed for the compacts sintered in helium.

**Effect of Sintering at Various Temperatures in**



**Helium on Compacts Pressed at 50 tsi:** In order to determine if gases were actually being evolved by the thermal decomposition of oxides contained in the powders, the oxygen content of compacts pressed at 50 tsi and sintered for 4 hr in helium at 1100°, 1200°, 1300°, and 1400°C was determined by means of vacuum-fusion analyses. A 4 hr time limit was chosen, because it was believed that the largest part of any thermal decomposition would have occurred in that length of time. As a basis for determining the original oxygen content of the compacts, vacuum-fusion analyses for oxygen were made on a compact pressed at 50 tsi and sintered in helium for 15 min at 800°C and also on a green compact of the same powder mixture. In conjunction with the vacuum-fusion analyses, the usual measurements were also made. These data are presented in Fig. 15.

The results of the vacuum-fusion analyses are expressed in terms of the original oxygen content of the green compacts (0.84 pct O) as determined by vacuum fusion. The fact that sintering 4 hr at 1100° and 1400°C in helium has eliminated 53 and 86 pct, respectively, of the original oxygen content of the compacts clearly indicates that gases are evolved during the sintering process.

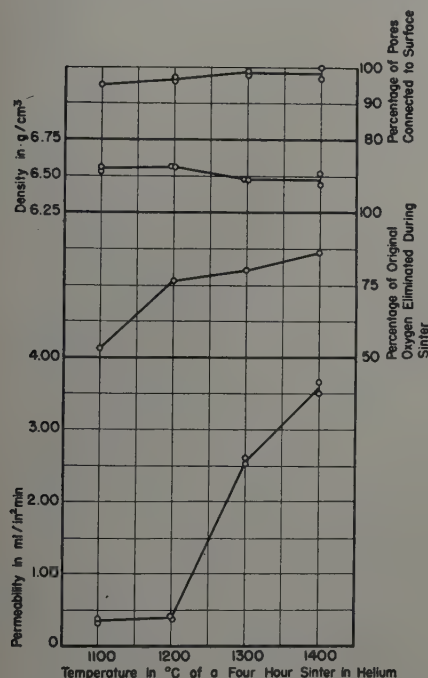


Fig. 15—Effect of sintering at various temperatures in helium on compacts pressed at 50 tsi.

In Fig. 15, the evolution of gases is also reflected by the rapid increase in permeability between 1200° and 1400°C accompanied by a small decrease in density and a small increase in the percentage of pores connected to the surface. The main reason for the difference between the properties of compacts sintered for 4 hr at 1200°C and for 4 hr at 1300° or 1400°C would seem to be due to the greater plasticity of the metal at the higher temperatures, because the difference in the amount of gas liberated at each of these three temperatures is obviously not enough to account for it. The fact that the expansion of individual pores has occurred during the sinter at 1200°C, but to a lesser extent than that at 1400°C, is shown by a comparison of Figs. 16 and 17.

**Effect of Heating Cobalt Powder to 1000°C in a Vacuum:** Because the cobalt powder had a hydrogen loss three times that for the iron powder (see Table III) and because its oxygen content by vacuum-fusion analysis was 1.04 pct compared to 0.41 pct

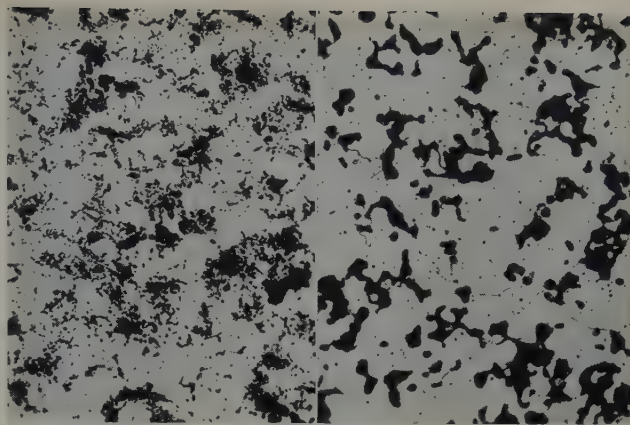


Fig. 16—Pressed at 50 tsi, sintered 4 hr at 1200°C in helium. X100.

Fig. 17—Pressed at 50 tsi, sintered 4 hr at 1400°C in helium. X100.

for the iron powder, a study was made of the evolution of gases upon heating from the cobalt powder alone. This was done by degassing in a vacuum a 4 g sample of cobalt powder for 2 hr at 225°C, sealing off the system at a vacuum of  $10^{-6}$  cm after degassing, and then measuring the pressure of the closed system as the cobalt powder was gradually heated (5°C per min) from 250° to 1000°C (the upper temperature limit of the apparatus). The results of this experiment, which are given in Fig. 18, show that rapid gas evolution occurs between 350° and 450°C and between 800° and 1000°C.

The volume of gas liberated upon heating to 1000°C was calculated to be 1.6 ml per g of cobalt powder. While this is an appreciable quantity of gas, it represents less than one fourth of the total gas available (7.3 ml per g) as calculated on the basis of the vacuum-fusion analysis (1.04 pct O). Vapor pressure and chemical solubility measurements showed that the gas evolved from the cobalt powder was largely carbon dioxide.

This carbon dioxide could be formed by the reaction between the carbon and oxides of the powders or by the release of chemisorbed gases. In their study of gas evolution on rise of temperature for carbonyl iron powder, Duftschmid, Schlecht, and Schubardt<sup>20</sup> found that the reaction between the carbon and iron oxide of the powders produced a major gas evolution at 450°C with the bulk of the gas being carbon dioxide with some carbon monoxide also present.

If all the carbon (0.069 pct) present in the cobalt powder were oxidized to carbon dioxide during the heating to 1000°C, then 1.3 ml of carbon dioxide per gram of powder would be produced. This leaves 0.3

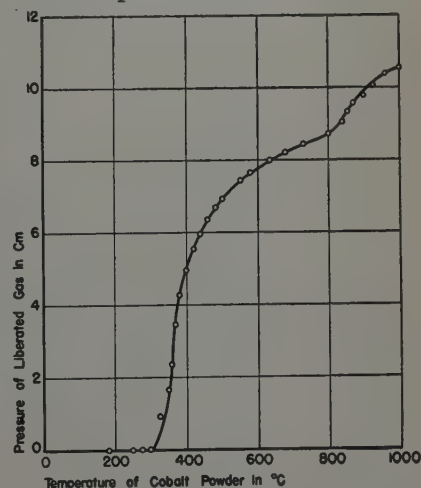


Fig. 18—Pressure of liberated gas vs. temperature for cobalt powder heated in a vacuum.

ml to be supplied by some other source, such as chemisorbed carbon dioxide.

The above discussion leads to the belief that the evolution of gas from the cobalt powder occurring at 400°C is largely due to the reduction of oxides by carbon in the powder and that the second evolution occurring at 800° to 1000°C is probably the result of the thermal decomposition of cobaltic oxide (decomposes at 895°C).

### Minimizing the Influence of Gases on Sintering Process

The final part of this investigation consisted of experiments that were designed to minimize or even eliminate, if possible, the influence of gases upon the sintering process.

*Effect of Reduction of Powder upon Influence of Gases during Sintering:* The most obvious method of minimizing the influence of gases upon the sintering process is to eliminate the source of these gases. An attempt was made to accomplish this purpose, first by reduction of the cobalt powder alone (because of its higher oxygen content) and then by reduction of both the iron and the cobalt powder just prior to compacting and sintering.

A series of compacts were prepared from cobalt powder, annealed in pure dry hydrogen for 1 hr at 600°C, and unannealed iron powder by pressing at 50 tsi and sintering for 30 min and for 24 hr at 1400°C. The properties of these compacts along with the properties of compacts fabricated in a similar manner from both unannealed cobalt and iron powder are listed in Table IV for comparison. The fact that the prior reduction of cobalt powder resulted in a lower permeability and a higher density for the compacts sintered 30 min at 1400°C would certainly seem to indicate that less pore expansion had occurred, and that, as a result, a higher density might be obtained for similar compacts sintered 24 hr at 1400°C. But as can be seen, this is not the case.

A glance at the microstructure of a compact prepared using the annealed cobalt powder and sintered for 30 min at 1400°C helps to resolve this difficulty, see Fig. 19. It should be noted that even though the hydrogen loss for the powders used in making the compact was reduced to one third of its original value by the prior reduction, the pores have still been enlarged sufficiently to interfere with the achievement of a high final density (24 hr at 1400°C).

In order that the maximum amount of gases might

be eliminated prior to sintering, both the iron and the cobalt powder were annealed for 1 hr at 600°C in pure dry hydrogen, and a series of compacts were pressed at 25 tsi and sintered 24 hr at 1400°C. As shown in Table IV, even this reduction treatment did not result in a higher final density.

*Effect of Variations in Sintering Cycle to Allow for Removal of Gases from Compacts:* Because the minimization of the deleterious effects of gases by variation in the sintering cycle had been successfully carried out by other investigators,<sup>12</sup> it was decided to use two such methods in order to eliminate the gases from the compacts before the inter pore channels could become sealed. The first method was to place the compacts in the furnace at 800°C and heat slowly (2.5° to 3° per min) from 800° to 1400°C in order to allow the oxides to be gradually reduced with the gaseous reduction products making their escape while the inter pore channels are still open. The second method was to place the compacts in the furnace at 800°C and hold at that temperature for 4 hr in order to provide for the maximum reduction of oxides before the sintering temperature was increased to 1400°C. At 800°C the gaseous reduction products can make their escape without disrupting the compact because the sintering action is relatively slow.

The results of these two experiments which are given in Table V show that both of the treatments described above have had a very beneficial effect in increasing the density. While the second method of varying the sintering cycle decreased the sintering time at 1400°C to 19 hr, it still resulted in higher final densities, even in the case of those compacts pressed at 25 tsi and having a low green density.

Fig. 20 shows the microstructure of a compact pressed at 25 tsi and placed in the furnace at 1400°C and sintered for 24 hr at that temperature, while Fig. 21 shows the microstructure of a compact pressed at 25 tsi and placed in the furnace at 800°C and given a slow heating rate from 800° to 1400°C before the final sinter at that temperature. A comparison of the two figures shows clearly that the use of a slow heating rate preceding the high temperature sinter results in both fewer and smaller pores. This in turn, is reflected in a higher density for this type of treatment.

### Summary

1—Data are presented to show the influence of various pressing and sintering conditions upon the

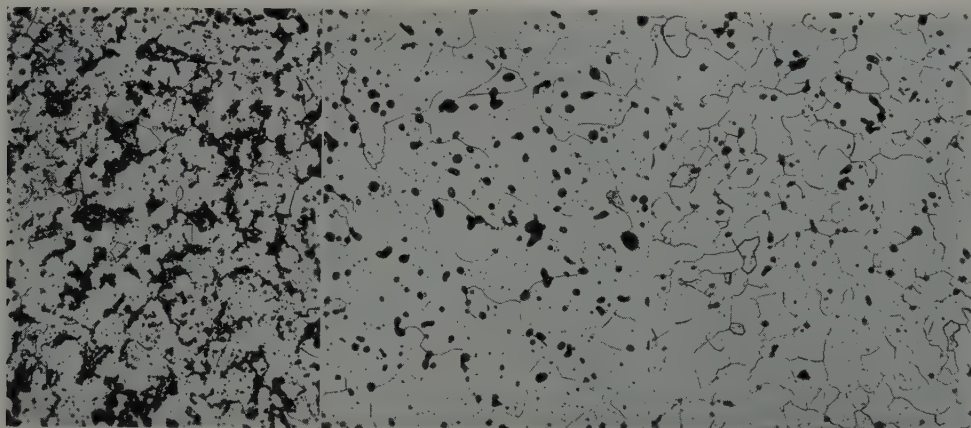


Fig. 19—Pressed at 50 tsi from annealed cobalt powder and unannealed iron powder. Sintered 30 min at 1400°C. X100.

Fig. 20—Pressed at 25 tsi, sintered 24 hr at 1400°C. X100.

Fig. 21—Pressed at 25 tsi. Slow heating rate from 800° to 1400°C preceding sinter at 1400°C. Total sintering time was 24 hr. X100.



Table IV. Comparison of Properties of Compacts Fabricated from Annealed and Unannealed Powders

| Powder Treatment                             |                                                | Compacting Pressure | Sintering Treatment | Permeability (Ml per In. <sup>2</sup> Min) | Density (G per Cm <sup>3</sup> ) |
|----------------------------------------------|------------------------------------------------|---------------------|---------------------|--------------------------------------------|----------------------------------|
| Annealed Co Powder<br>Unannealed Fe Powder   | Total H <sub>2</sub> loss for both was 0.3 pct | 50 tsi              | 30 min at 1400°C    | 0.18                                       | 6.75                             |
|                                              |                                                |                     |                     | 0.25                                       | 6.76                             |
|                                              |                                                |                     |                     |                                            |                                  |
|                                              |                                                |                     |                     |                                            |                                  |
| Unannealed Co Powder<br>Unannealed Fe Powder | Total H <sub>2</sub> loss for both was 0.9 pct | 50 tsi              | 24 hr at 1400°C     | 0.63                                       | 6.56                             |
|                                              |                                                |                     |                     | 0.57                                       | 6.56                             |
|                                              |                                                |                     |                     |                                            |                                  |
|                                              |                                                |                     |                     |                                            |                                  |
| Annealed Co Powder<br>Unannealed Fe Powder   | Total H <sub>2</sub> loss for both was 0.3 pct | 50 tsi              | 24 hr at 1400°C     |                                            | 7.570                            |
|                                              |                                                |                     |                     |                                            |                                  |
|                                              |                                                |                     |                     |                                            |                                  |
|                                              |                                                |                     |                     |                                            |                                  |
| Unannealed Co Powder<br>Unannealed Fe Powder | Total H <sub>2</sub> loss for both was 0.9 pct | 50 tsi              | 24 hr at 1400°C     |                                            | 7.571                            |
|                                              |                                                |                     |                     |                                            | 7.537                            |
|                                              |                                                |                     |                     |                                            |                                  |
|                                              |                                                |                     |                     |                                            |                                  |
| Annealed Co Powder<br>Annealed Fe Powder     |                                                | 25 tsi              | 24 hr at 1400°C     |                                            | 7.665                            |
|                                              |                                                |                     |                     |                                            | 7.665                            |
|                                              |                                                |                     |                     |                                            | 7.645                            |
|                                              |                                                |                     |                     |                                            |                                  |
| Unannealed Co Powder<br>Unannealed Fe Powder |                                                | 25 tsi              | 24 hr at 1400°C     |                                            | 7.661                            |
|                                              |                                                |                     |                     |                                            | 7.654                            |
|                                              |                                                |                     |                     |                                            |                                  |
|                                              |                                                |                     |                     |                                            |                                  |

permeability, density, and percentage of pores connected to the surface of Fe-Co powder compacts. This data has led to a study of the effect of evolved gases on the sintering process and to a successful minimization of the influence of such gases.

2—It has been shown that a density study does not always afford a reliable means of following the sintering process in powder compacts. On the other hand, liquid permeability measurements have indicated changes occurring in the sintering process not revealed by density measurements. Permeability has been shown to be a fairly good measure of the relative pore sizes of powder compacts, as well as the degree to which these pores are interconnected. While a metallographic study offers a reliable check on the relative pore sizes, it is lacking in that it does not show the degree of interconnection of the pores. The pore volume measurements introduced here offer a new method of determining the percentage of the total pores in a compact that are actually connected to the surface.

3—The experiments performed indicate that the role of gases during the initial stages of the sintering

Table V. Effect of Variations in Sintering Cycle upon Final Density of Compacts Pressed at 25, 50, and 75 tsi

| Compacting Pressure (Tsi) | Sintered 24 Hr at 1400°C | Slow Heating Rate (2.5°-3° Per Min) from 800° to 1400°C. Held at 1400°C Until Total Sintering Time Was 24 Hr | Held at 800°C for 4 Hr. Rapid Heating Rate (10°C Per Min) from 800° to 1400°C. Held at 1400°C Until Total Sintering Time Was 24 Hr |
|---------------------------|--------------------------|--------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|
| 25                        | 7.661                    | 7.863                                                                                                        | 7.771                                                                                                                              |
|                           | 7.654                    | 7.859                                                                                                        | 7.773                                                                                                                              |
|                           |                          | 7.857                                                                                                        | 7.766                                                                                                                              |
| 50                        | 7.525                    | 7.843                                                                                                        | 7.886                                                                                                                              |
|                           | 7.553                    | 7.845                                                                                                        | 7.879                                                                                                                              |
|                           |                          | 7.848                                                                                                        | 7.881                                                                                                                              |
| 75                        | 7.362                    | 7.785                                                                                                        | 7.836                                                                                                                              |
|                           | 7.391                    | 7.793                                                                                                        | 7.816                                                                                                                              |
|                           |                          | 7.757                                                                                                        | 7.825                                                                                                                              |

process have an important influence upon the final density of compacts sintered to achieve theoretical density. In this connection, high compacting pressures, rapid heating rates, and high sintering temperatures exaggerate the effect of evolved gases and promote the formation of large initial pores which are eliminated during continued sintering only with difficulty.

4—A density close to that for the fused alloy (97.5 pct) has been obtained for 50 pct Fe-50 pct Co powder compacts by providing for the escape of liberated gases before appreciable sintering has occurred.

5—The results of this investigation should prove of interest to powder metallurgists concerned with the production of very high density materials or with the production of parts having a controlled porosity, such as bearings and filters.

#### Acknowledgments

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# Constitution and Precipitation-Hardening Properties of Copper-Rich Copper-Tin-Beryllium Alloys

by R. A. Cresswell and J. W. Cuthbertson

THE constitution of Cu-rich alloys with 1.5 to 13.5 pct Sn and 0.25 to 3.0 pct Be and the precipitation-hardening characteristics of alloys with 1.5 to 13.5 pct Sn and 0.25 to 1.0 pct Be have been examined.

The hardness and tensile strength of the alloys examined increase markedly after solution treatment at 700°C followed by heat treatment at temperatures between 200° and 450°C. By a combination of cold work and heat treatment, hardness values similar to those exhibited by commercial Be-Cu alloys containing 2.25 pct Be can be obtained with ternary alloys containing 9 pct Sn and 0.75 pct Be and containing 10 pct Sn and 0.5 pct Be. Marked hardening effects occur with alloys containing even less beryllium. By heat treatment alone, a hardness value of 310 diamond pyramid hardness can be obtained from an alloy containing 10 pct Sn and 0.75 pct Be. Preliminary tensile tests have shown that an ultimate tensile strength of 110,000 psi with an elongation of 23 pct is obtainable by precipitation hardening an alloy with 8 pct Sn and 0.75 pct Be.

The precipitation-hardening process has been followed microscopically for certain alloys and the inference is that, while the initial hardening effect is probably explained by the precipitation of the  $\beta'$  phase of the Cu-Be system, further hardening, proceeding at a much slower rate, also occurs, apparently as a result of precipitation of phases of the Cu-Sn system, particularly precipitation of the  $\epsilon$  phase at temperatures below 350°. The presence of the  $\epsilon$  phase of the Cu-Sn system in certain alloys at temperatures below 350°C has been confirmed.

Tin-bronzes are widely used in engineering applications where a combination of high strength and good resistance to corrosion is wanted. The maximum strength is induced in these alloys by cold working, and it would be an advantage for many purposes if high strength could be achieved alternatively by an age-hardening process. While Cu-Sn alloys have a good fatigue resistance they can be surpassed in this respect by Cu-Be, but the use of the latter alloy is limited by its high cost. If, by adding beryllium to tin-bronze, the properties of the respective binary alloys could to some extent be combined, a most attractive alloy should result.

As pointed out by Raynor,<sup>1</sup> beryllium is on the borderline of the zone of favorable size factors for copper, and the solid solubility of beryllium in copper is consequently much more restricted than if the size factor were strongly favorable. The size factor is sufficiently favorable, however, to permit an increase in solid solubility with rise in temperature, and there is thus a composition range in which Cu-

Be alloys are susceptible to hardening by precipitation heat treatment. Although the  $\alpha$  phase of the Cu-Sn system is similarly susceptible to precipitation treatment, the time necessary to establish equilibrium in commercial alloys of this type is usually so great that age hardening becomes impracticable.

The addition of beryllium to Cu-Sn alloys would appear to offer a means of conferring on the latter useful age-hardening properties. Masing and Dahl<sup>2</sup> and others have, in fact, shown that the addition of beryllium to Cu-Sn  $\alpha$  solid solutions renders these alloys susceptible to precipitation hardening and after such hardening confers on them an encouraging improvement in physical properties. If this improvement could be achieved by the addition of substantially smaller amounts of beryllium than are customarily found in binary Cu-Be alloys, the ternary alloys should possess economic advantages which might make them more attractive than the binary alloy for some applications.

## Binary Systems

**Copper-Tin:** The constitution of these alloys is now reasonably well known and is summarized in the equilibrium diagram published by Raynor.<sup>3</sup>

The following observations, due to Raynor,<sup>1</sup> on the structure of those phases of the Cu-Sn system that are likely to be found in the ternary alloy system will facilitate the subsequent discussion on the examination of that system. The  $\beta$  phase is an electron compound at the electron-atom ratio 3:2 and has a body-centered cubic crystal structure. This phase is stable only down to 586°C, at which temperature it decomposes eutectoidally into the  $\alpha$  and  $\gamma$  phases. The  $\gamma$  phase has a structure that is also based on the cubic system. This phase is stable down to 520°C, at which temperature it decomposes eutectoidally into the  $\alpha$  and  $\delta$  phases. The  $\delta$  phase is an electron compound ( $\text{Cu}_{21}\text{Sn}_8$ ) which has a crystal structure analogous to that of  $\gamma$  brass. This phase is stable from 590° to 350°C; on prolonged annealing at the latter temperature it breaks down into a mixture of the  $\alpha$  and  $\epsilon$  phases. The  $\epsilon$  phase is an electron compound ( $\text{Cu}_3\text{Sn}$ ) having the electron-atom ratio 7:4. Its structure may be regarded as a superlattice based on the close-packed hexagonal system. This phase is stable from 676°C to room temperature.

The primary solid solubility of tin in copper increases to a maximum of 15.8 pct as the temperature falls from that of the peritectic reaction to 586°C. The solid solubility remains constant from 586° to 520°C. At lower temperatures the solubility decreases progressively. Below 350°C the fall in solubility is pronounced and is associated with the precipitation of the  $\epsilon$  phase. This precipitation is very sluggish and does not normally occur under service conditions.

**Copper-Beryllium:** The Cu-Be system has been investigated by Borchers<sup>4</sup> and others. Raynor<sup>5</sup> summarized the present state of information on it.

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The solid solubility of beryllium in copper does not exceed 2.1 pct. Beyond the  $\alpha$  range increase in beryllium content up to about 12 pct leads to the appearance of first the  $\beta$  phase and subsequently the  $\beta'$  phase (the latter phase is designated  $\gamma$  by Borchers). The  $\beta$  and  $\beta'$  phases both have body-centered cubic structures, the former being disordered and the latter ordered. Hume-Rothery, Reynolds, and Raynor<sup>9</sup> consider that both of these phases are probably derived from the same 3:2 electron compound. The  $\beta$  phase decomposes eutectoidally at 575°C giving the  $\alpha$  and  $\beta'$  phases.

**Tin-Beryllium:** So far as could be traced no information has been published on the Sn-Be system. Raynor considers that the size factor relationships in this case are unfavorable.

### Ternary System

The first work carried out on the Cu-Sn-Be system was done by Masing and Dahl in 1929.<sup>2</sup> They determined the limits of the  $\alpha$  phase at 750°C and examined the possibilities of precipitation hardening in these alloys. Rowland and Upthegrove<sup>7</sup> have pointed out, however, that owing to insufficient annealing the specimens on which Masing and Dahl based their conclusions were not in equilibrium and the results of the latter's findings in regard to the constitution diagram are thus open to criticism. Rowland and Upthegrove have examined the structure of Cu-Sn-Be alloys containing up to 1 pct Be. They have not, however, studied the age-hardening properties of these alloys in detail, and since in their investigation they used the older type of Cu-Sn constitution diagram based on the work of Heycock and Neville, they appear to have overlooked the transformation of the  $\delta$  phase of that system at approximately 350°C. In the light of later work on the Cu-Sn system it would seem the  $\beta'$ ,  $\beta + \gamma$ , and  $\gamma$  fields reported by Rowland and Upthegrove can almost certainly be identified with one continuous  $\gamma$  field.

### Scope of Present Investigation

In planning this investigation the general form of Rowland and Upthegrove's diagram and the results of their thermal analyses were accepted, and it was decided only to consider those sections of the system which, in view of the information that has become available since these investigators published their results, might justify re-examination. In view of these uncertainties it was deemed advisable to redetermine certain parts of the ternary diagram in order to settle what phases are most likely to be precipitated on heat treatment of alloys near the  $\alpha$  phase boundary, i.e., alloys in which the maximum degree of precipitation hardening is to be expected.

The boundaries of selected isothermal sections of the ternary model were determined by microscopical examination of annealed and quenched specimens. The effects of heat treatment on selected alloys were examined and a limited study was made of the mechanical properties of these alloys.

### Experimental Procedure

In all, 68 different alloys were prepared. Of these 58 were made from electrolytic copper, Chempur tin, and a Cu-Be master alloy containing 4 pct Be. The remaining 10 alloys, which were used to settle any doubtful questions in the constitution work, were made from raw materials that were spectrographically standardized and of very high purity.

The analyses of the copper, tin, and master alloy

Table I. Analyses of Raw Materials

| Material                 | Impurity Content                                                             |              |               |               |
|--------------------------|------------------------------------------------------------------------------|--------------|---------------|---------------|
| Copper.....              | Fe 0.005 pct                                                                 | As 0.001 pct | Cd 0.001 pct  |               |
|                          | CuO 0.04 pct                                                                 | approx.      |               |               |
| Tin.....                 | Typical analysis for Chempur tin:                                            |              |               | Fe 0.0013 pct |
|                          | Pb 0.0027 pct                                                                | Sb 0.003 pct | Bi 0.0006 pct |               |
|                          | Cu 0.0005 pct                                                                | As nil.      |               |               |
| Cu-Be Master Alloy ..... | 0.3 pct total impurity, mainly Fe, Al and Si in approximately equal amounts. |              |               |               |

are given in Table I, and the tin and beryllium contents of the prepared alloys are reported in Table II. All samples were analyzed for tin content by precipitation with tannin and for beryllium content by precipitation with 8-hydroxy quinoline and ignition to oxide, traces of iron and aluminium being removed first. The impurity content of selected alloys was determined and the total amount of impurity found did not exceed 0.1 pct. The average silicon content was 0.03 to 0.05 pct and traces of iron and aluminium were detected.

In preparing the majority of the alloys for the constitution work, the metals were melted in a salamander crucible heated in an electric furnace of the silicon-carbide resistor type. During melting, a stream of oxygen-free nitrogen was passed through the furnace and melting was carried out as quickly as possible. The usual procedure in making up alloys of low beryllium content was first to melt the copper and bring its temperature rapidly to about 1300°C and then to add the tin and master alloy which were first preheated. The normal casting temperature was 1150°C. Before casting, the melts were stirred with a carbon rod and casting was effected through a preheated tundish into a chill mold  $\frac{3}{4}$  in. in diam preheated to 200°C. In the case of the alloys of higher beryllium content, the total charge was placed in the crucible at the outset and melting and casting were carried out as before. The usual weight of the melts prepared in the electric furnace was 250 g. Experience indicated that provided the melting was done quickly there was no significant increase in the silicon content of alloys prepared in this way. With prolonged heating the silicon in the alloy may increase as a result of reduction of the silica in the crucible by the beryllium in the melt.

Larger melts were required for studying precipitation hardening and the mechanical properties of the alloys, and these were prepared as follows. Melting was done in a gas-fired injector furnace. The

Table II. Analyses of Alloys

| Alloy No. | Sn, Pct | Be, Pct | Alloy No. | Sn, Pct | Be, Pct | Alloy No. | Sn, Pct | Be, Pct |
|-----------|---------|---------|-----------|---------|---------|-----------|---------|---------|
| 1         | 1.5     | 0.95    | 24        | 3.85    | 1.88    | 47†       | 8.45    | 2.80    |
| 2         | 1.5     | 1.45    | 25        | 4.25    | 2.49    | 48†       | 9.1     | 0.21    |
| 3         | 1.5     | 1.85    | 26        | 5.2     | 0.24    | 49*       | 9.15    | 0.48    |
| 4         | 1.9     | 0.18    | 27        | 4.65    | 0.50    | 50*       | 8.8     | 0.75    |
| 5         | 2.1     | 0.47    | 28        | 4.7     | 0.87    | 51        | 8.95    | 1.52    |
| 6*        | 1.9     | 0.70    | 29        | 5.3     | 1.10    | 52†       | 9.3     | 1.80    |
| 7         | 2.05    | 1.50    | 30        | 4.9     | 2.29    | 53†       | 9.39    | 0.26    |
| 8*        | 2.5     | 0.48    | 31        | 5.9     | 0.15    | 54†       | 9.54    | 0.21    |
| 9*        | 2.6     | 0.95    | 32        | 6.15    | 0.55    | 55*       | 9.8     | 0.17    |
| 10        | 2.4     | 1.30    | 33        | 5.75    | 0.79    | 56*       | 10.0    | 0.47    |
| 11        | 2.65    | 1.65    | 34        | 6.2     | 2.77    | 57*       | 9.88    | 0.73    |
| 12        | 2.45    | 1.90    | 35†       | 6.35    | 2.85    | 58        | 10.25   | 0.87    |
| 13        | 2.9     | 0.20    | 36        | 7.25    | 1.0     | 59        | 9.95    | 2.06    |
| 14†       | 3.19    | 0.31    | 37        | 7.05    | 1.60    | 60        | 11.05   | 0.13    |
| 15        | 3.1     | 2.05    | 38        | 7.25    | 1.95    | 61*       | 11.15   | 0.47    |
| 16*       | 3.5     | 0.52    | 39        | 7.1     | 2.75    | 62*       | 10.75   | 0.77    |
| 17†       | 3.6     | 1.15    | 40        | 7.65    | 1.10    | 63*       | 11.4    | 0.73    |
| 18        | 3.5     | 1.90    | 41*       | 7.75    | 0.67    | 64*       | 12.2    | 0.21    |
| 19        | 3.85    | 0.005   | 42        | 8.45    | 0.96    | 65*       | 12.25   | 0.47    |
| 20        | 4.1     | 0.53    | 43        | 7.75    | 2.45    | 66*       | 13.35   | 0.47    |
| 21*       | 3.9     | 0.97    | 44        | 8.15    | 2.88    | 67*       | 12.75   | 0.73    |
| 22†       | 3.7     | 0.80    | 45†       | 8.64    | 0.27    | 68*       | 13.55   | 0.24    |
| 23        | 4.0     | 1.73    | 46        | 8.55    | 1.05    | 69        | 14.55   |         |

\* Alloys melted in the gas-fired injector furnace.

† Alloys made up from spectrographically standardized materials.

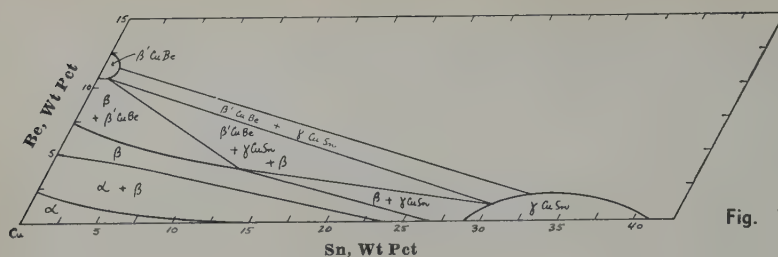


Fig. 1a—700°C isothermal diagram, general form.

Fig. 1b—700°C isothermal diagram, alpha phase boundary.

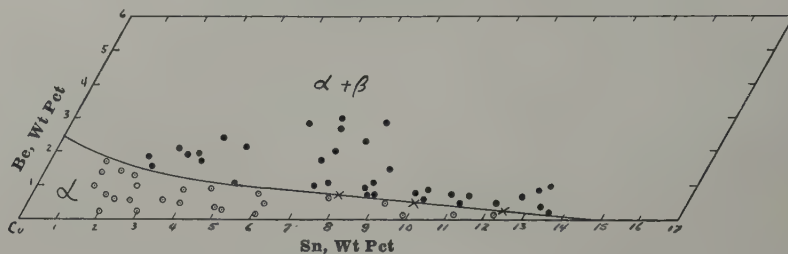


Fig. 2a—600°C isothermal diagram, general form.

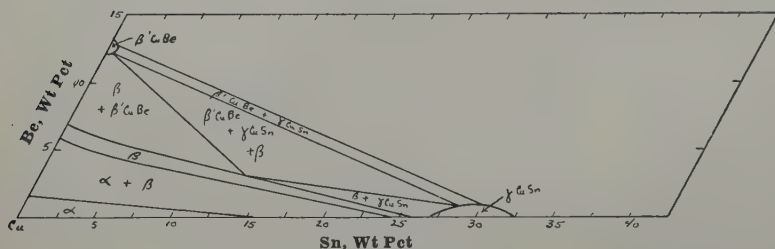


Fig. 2b—600°C isothermal diagram, alpha phase boundary.

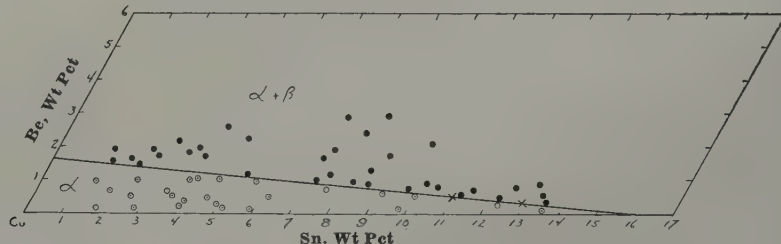
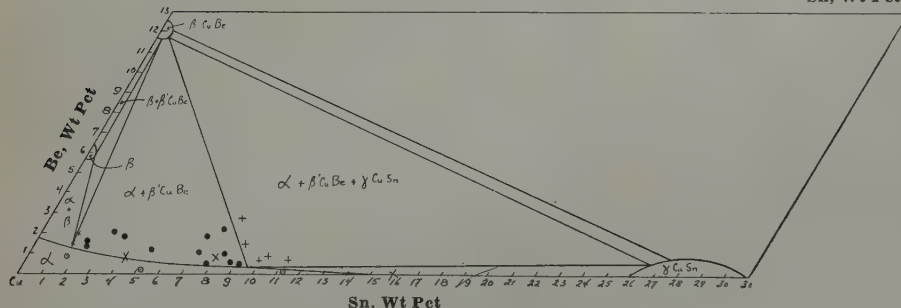


Fig. 3—580°C isothermal diagram.



copper was melted under an oxidizing flux consisting of equal parts of cupric oxide, borax, and sand, and was raised to a temperature of 1250° to 1300°C. The flux was thickened with sand and removed. The copper was deoxidized with 15 pct phosphor-copper and the Sn and Cu-Be alloy were added in that order. The melts were poured at 1150°C into a cast iron mold measuring 10x2x1½ in. preheated at 150°C. Slow pouring was insured by the use of a tundish having an outlet orifice ⅛ in. in diam. The weight of the castings made in this way was approximately 1200 g. Before use, these castings were annealed at 700°C for 15 hr. While these samples were prepared primarily for the purposes mentioned above, melts thus made that on analysis were found to be substantially free from phosphorus were also used to provide additional data on alloy constitution, particularly in the higher tin regions.

#### Preparation of Microspecimens

The cast alloys were annealed for 2 hr at 700°C, hammered while hot, reannealed at 700°C for 16 hr,

and water quenched. Drillings for chemical analysis were taken from the bottom of each ingot and the specimens for microscopic examination were cut from the portion just above. No variation in composition along the lengths of the castings was detectable, and it is considered that the chemical analyses correspond very closely with that of the microspecimens taken from adjacent parts of the castings. Six batches of microspecimens were cut from castings of the desired compositions, and all of the specimens were annealed at 700°C for 96 hr. At the end of this time the first batch of specimens was withdrawn and water quenched. The temperature of the annealing furnace was then slowly lowered to 600°C and maintained at this temperature for a further 96 hr, following which the second batch of specimens was water quenched. This procedure was repeated, with progressive decrease in the intermediate cooling rate, at 580°, 500°, and 400°C. The final batch of specimens was held at 300°C for 168 hr before quenching. On examination of the samples in this batch it was found that soaking for 168 hr was not



## Legend

- — Single-phase alloys
- — Two-phase alloys
- + — Three-phase alloys
- × — Points on Rowland and Upthegrove's alpha phase boundary

Fig. 4—500°C isothermal diagram.

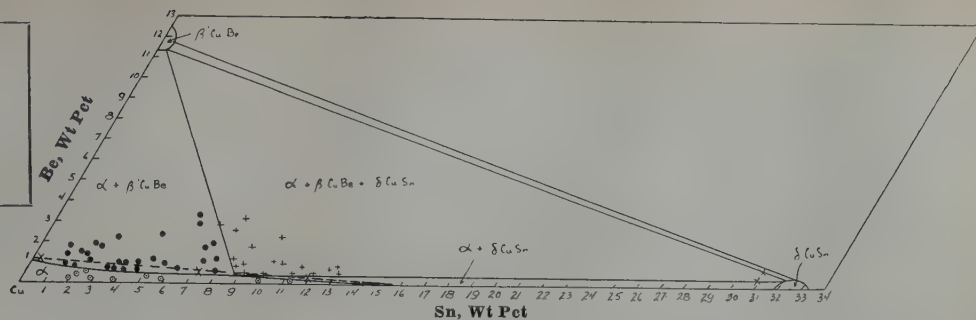


Fig. 5—400°C isothermal diagram.

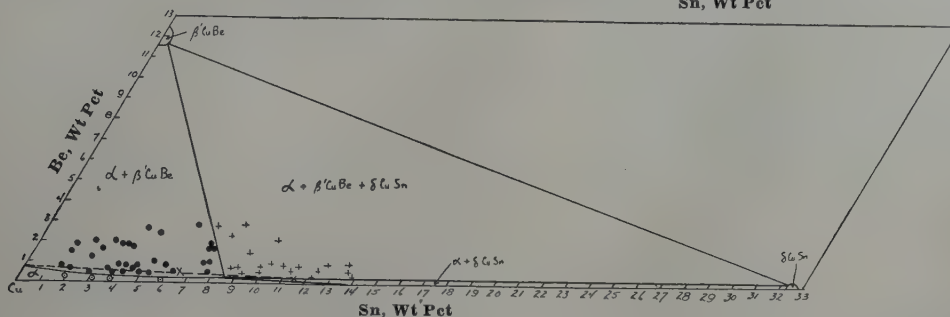
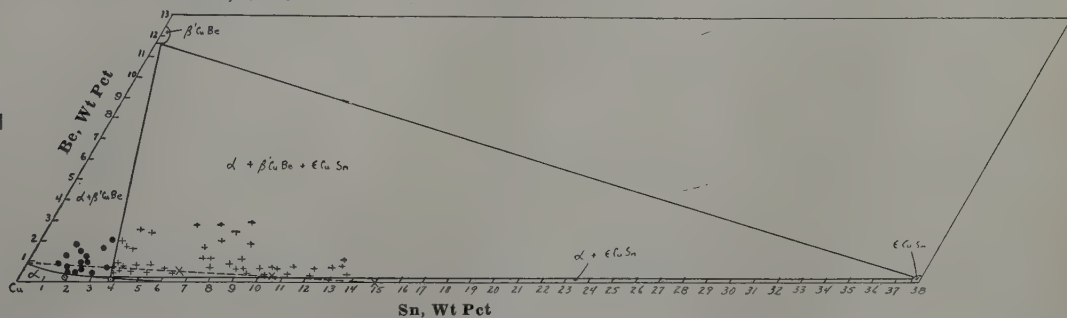


Fig. 6—300°C isothermal diagram.



sufficient to establish equilibrium in all of the alloys, and selected alloys near phase boundaries were therefore reannealed for a further 60 days to insure that equilibrium was established.

The microsections were prepared by hand polishing on Selvyt cloth moistened with Silvo metal polish and soap, and were etched in alcoholic ferric chloride or preferably in alkaline cuprammonium chloride. The latter etchant was found to give excellent phase differentiation in the majority of the three-phase alloys.

## Results of the Constitution Investigation

The ternary isothermals at 700°, 600°, 580°, 500°, 400°, and 300°C are shown in Figs. 1 to 6.\* For

purposes of comparison some of the points on the phase boundaries of Rowland and Upthegrove's diagram have been included.

**Sections at 700° and 600°C:** It is confirmed, Figs. 1 and 2, that the  $\beta$  phases of the Cu-Sn and Cu-Be systems form a continuous series of solid solutions and that at these temperatures alloys in the copper corner of the diagram consist of  $\alpha$ , or  $\alpha + \beta$ . The  $\beta$  phase is retained by quenching and is easily recognizable as white island in the darker  $\alpha$  matrix. The phase boundaries at these temperatures are in close agreement with those of Rowland and Upthegrove.

\* In Figs. 1 to 6 the abbreviation CuSn, etc., merely indicates the constituent metals and not the compositions of the respective phases.

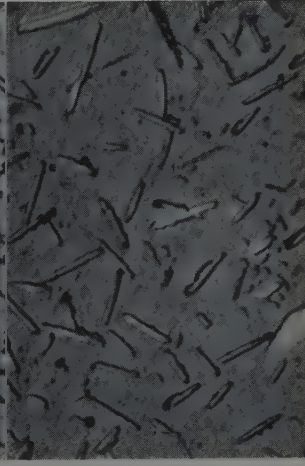
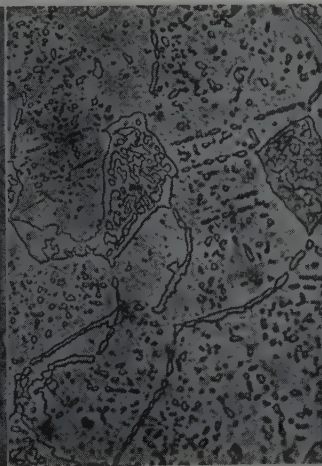
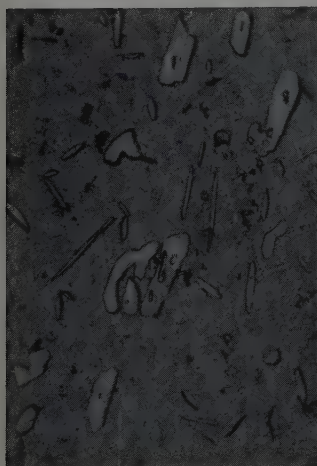


Fig. 7—Equilibrium structure at 580°C of alloy No. 12, 2.5 pct Sn-2 pct Be. X750.

Fig. 8—Equilibrium structure at 500°C of alloy No. 61, 11 pct Sn-0.5 pct Be. X500.

Fig. 9—Equilibrium structure at 500°C of alloy No. 57, 10 pct Sn-0.75 pct Be. X2000.

Fig. 10—Equilibrium structure at 500°C of alloy No. 41, 8 pct Sn-0.75 pct Be. X500.

Nominal compositions are given for these and all other micrographs.





Fig. 11—Equilibrium structure at 300°C of alloy No. 68, 13.5 pct Sn-0.25 pct Be. X1750. Fig. 12—Equilibrium structure at 300°C of alloy No. 22, 4 pct Sn-1 pct Be. X2000.

**Section at 580°C:** Owing to the transformation at 586°C of the  $\beta$  phase of the Cu-Sn system into  $\alpha + \gamma$ , this section, Fig. 3, shows a marked change from the one at 600°C. Pseudobinary systems are formed between the  $\alpha$  and the  $\beta'$  phases of the Cu-Be system and between the  $\gamma$  phase of the Cu-Sn system and the  $\beta'$  phase of the Cu-Be system. One three-phase field appears between the  $\alpha$ ,  $\beta$ , and  $\beta'$  phases of the Cu-Be system and another between the  $\alpha$ ,  $\beta'$  CuBe, and  $\gamma$  phase of the Cu-Sn system. In the  $\alpha + \beta'$  CuBe +  $\gamma$  Cu-Sn field, the islands that were originally  $\beta$  now consist of  $\gamma$  Cu-Sn and/or  $\beta'$  CuBe and  $\alpha$ , and have become coarse in structure. The  $\gamma$  Cu-Sn phase is light gray in color and similar in form to the  $\beta$  phase of the Cu-Sn system. The  $\beta'$  CuBe phase, designated  $\theta$  by Rowland and Upthegrove, is readily recognized by its white color and acicular form. Fig. 7 shows the equilibrium structure of an alloy containing approximately 2.5 pct Sn and 2 pct Be and reveals needles of CuBe and islands of Cu-Sn in a matrix of  $\alpha$ .

**Sections at 500° and 400°C:** In these sections, Figs. 4 and 5, the  $\gamma$  phase of the Cu-Sn system is no longer present having undergone a eutectoid inversion into  $\alpha + \delta$ . At these lower temperatures the  $\alpha$  solid solubility is reduced and  $\beta'$  CuBe or  $\delta$  Cu-Sn (or both) phases precipitate from the  $\alpha$ . The  $\delta$  phase of the Cu-Sn system is precipitated from the  $\alpha$  at the grain boundaries and within the grains themselves and is readily distinguished by its bluish-gray color. The  $\beta$  phase no longer exists and is replaced by a more complex structure consisting of  $\alpha$  and either  $\beta'$  CuBe or  $\delta$  Cu-Sn, or both, depending on the composition (see Figs. 8 to 10).

The range of  $\alpha$  solid solubility at 500°C was found

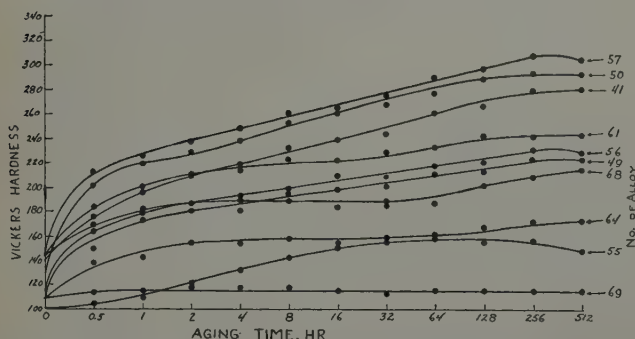


Fig. 13—Hardness-time curves of rolled specimens annealed at 700°C, water quenched, and aged at 250°C.

to be more restricted than is indicated in Rowland and Upthegrove.

**Section at 300°C:** Only a trace of the  $\delta$  phase was observed in specimens annealed at 300°C for 8 weeks, Fig. 6: the  $\delta$  phase had practically all decomposed to give  $\alpha$  and  $\epsilon$ , Figs. 11 and 12. Some  $\epsilon$  is also precipitated from the  $\alpha$  in form of very small gray particles, some of which are barely resolved at a magnification of 2000. X-ray examination confirmed the existence of this phase in alloys in equilibrium but failed to detect its presence in alloys annealed for only two weeks.

The restriction in  $\alpha$  solid solubility at this temperature was found to be very marked, and diverged considerably from that observed by Rowland and Upthegrove.

## General Discussion

All phase boundaries were found to shift toward lower tin contents with increase in beryllium content. Also, the  $\alpha$  field of the ternary system was found to decrease in area with decrease in temperature below 600°C. This decrease becomes marked at temperatures below the  $\gamma \rightarrow \alpha + \delta$  transformation of the Cu-Sn system and is still more marked below the temperature of the  $\delta \rightarrow \alpha + \epsilon$  transformation of the Cu-Sn system. This decrease in solubility accounts for the susceptibility to precipitation hardening in certain alloys of the ternary system noted by Masing and Dahl. The effect of composition and temperature on the limits of  $\alpha$  solid solubility can be appreciated from the figures given in Table III.

## Precipitation Hardening of Cu-Sn-Be Alloys

Masing and Dahl showed that Cu-Sn-Be alloys of suitable composition could be heat treated in the same way as binary Cu-Be alloys and demonstrated that the hardness of ternary alloys could be very considerably increased by aging after solution treatment. Further, aging was shown to be possible at temperatures below the recrystallization temperature, and the effect of cold working and precipitation hardening could therefore be superimposed.

The majority of Masing and Dahl's alloys contained 1.25 pct Be, or more. As such alloys would offer little economic advantage over the standard binary alloy containing around 2 pct Be, it was decided to investigate alloys of lower beryllium content. The alloys investigated had nominal contents of 2.0 to 13.5 pct Sn and 0.25 to 1.0 pct Be.

Rolled specimens were mainly used for the study of precipitation hardening. The melting procedure adopted in making ingots for this part of the work has already been described. After annealing the ingots at 700°C for 15 hr attempts were then made to hot roll them, but serious cracking occurred with all compositions. Cold rolling was therefore substituted and a number of ingots were successfully cold rolled down to a thickness of 0.1 in. Some ingots cracked badly in the early stages of rolling, especially those of alloys containing a large amount of a second phase. By adopting certain expedients the

Table III. Limiting Tin Content of  $\alpha$  Solid Solutions

| Temperature, °C | Tin, Pct       |               |             |
|-----------------|----------------|---------------|-------------|
|                 | At 0.25 Pct Be | At 0.5 Pct Be | At 1 Pct Be |
| 700             | 12.7           | 9.6           | 5.4         |
| 600             | 13.0           | 9.3           | 4.7         |
| 500             | 9.3            | 2.5           |             |
| 400             | 4.4            | 1.0           |             |
| 300             | 1.6            | 0.4           |             |



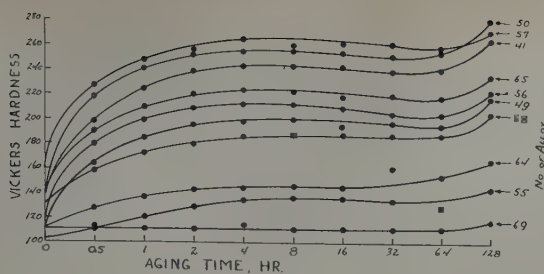


Fig. 14—Hardness-time curves of rolled specimens annealed at 700°C, water quenched, and aged at 300°C.

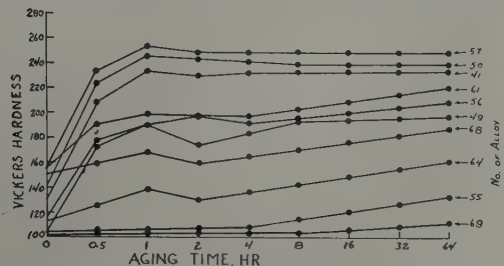


Fig. 15—Hardness-time curves of rolled specimens annealed at 700°C, water quenched, and aged at 350°C.

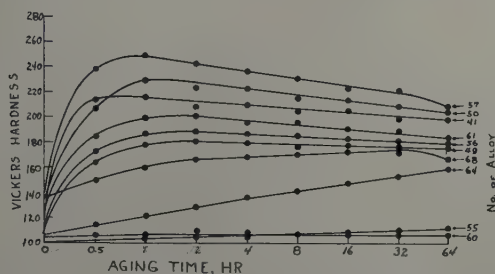


Fig. 16—Hardness-time curves of rolled specimens annealed at 700°C, water quenched, and aged at 400°C.

tendency to cracking was reduced and in many cases cracking was completely eliminated.

The procedure finally adopted was as follows: The annealed ingots were cold rolled to a reduction of 30 to 40 pct in several passes; they were then annealed for 15 min and again cold rolled as before. The whole procedure was repeated until a thickness of 0.1 in. was attained. In this way alloys Nos. 6, 8, 9, 16, 20, 21, 41, 49, 50, 55, 56, 57, 61, 64, and 68 selected from the list given in Table II were successfully worked. For comparison, a binary tin-bronze containing 14.55 pct Sn was also prepared, and no trouble was experienced in working this alloy. The remaining alloys selected, namely, Nos. 62, 63, 65, 66, and 67, contained a large amount of a second phase in addition to the  $\alpha$  constituent, and these alloys cracked severely on cold working.

All specimens were subjected to a solution heat treatment at 700°C before aging. This temperature is below the solidus for all of the alloys examined. Equilibrium was established in worked alloys after annealing at this temperature for 16 hr. Aging after solution treatment was carried out at 250°, 300°, 350°, 400°, and 450°C, the times of treatment being 0.5, 1, 2, 4, 8, 16, 32, and 64 hr: In addition, at 250°C the effect of prolonged aging for 128 and 256 hr was studied. Some alloys containing low amounts of tin and beryllium were also examined after aging at only 200°C.

**Effect of Aging on Hardness:** Hardness tests were made with a Vickers machine using a load of 50 kg and a time of application of 15 sec. At least three impressions were made for each test. The results obtained on rolled material were consistent, but

there was some scatter in the hardness readings for as-cast samples.

The relationship between hardness and time of aging is shown in Figs. 13 to 16. For all ternary alloys aging at 250°C causes a rapid increase in hardness during the first hour, after which the hardness increases at a steady rate that is almost directly proportional to the logarithm of the time. The latter increase continues up to 256 hr. After 256 hr alloy No. 57 had a hardness of 310, which is the maximum figure recorded for any preannealed alloy. On aging at 300°C, the increase in hardening during the first hour is greater than at 250°C: On further aging at 300°C, the hardness remains fairly constant except in the case of alloys low in tin and beryllium for which the hardness increases progressively.

On aging at 350°C, the hardness of alloys containing 0.75 pct Be reaches a maximum after about 1 hr and thereafter remains substantially constant. Alloys of lower beryllium content continue to increase in hardness after 1 hr, but less markedly than when aged at 250° and at 350°C. On aging at 400°C and at 450°C, the hardness after the first hour of alloys with 0.5 to 0.75 pct Be diminishes with time; alloys with 0.25 pct Be show a progressive increase in hardness, as in the lower temperature treatments.

The extent to which hardness increases on aging appears to be determined almost entirely by the beryllium content of the alloys. Increase in the tin content of the alloys raises the general level of the hardness-aging time curves but does not significantly affect age hardening. Except in the case of alloys high in tin and beryllium, where the maximum hardness is reached after aging at 400° to 450°C, the remaining alloys attain their greatest hardness after aging at 250°C for 256 hr.

It was observed that many of the alloys examined could be cold worked in the solution-treated condition and the effect of age hardening superimposed on work hardening was next investigated. Figs. 17

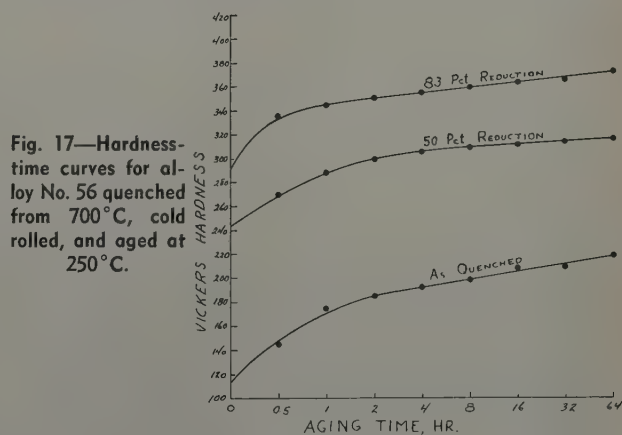


Fig. 17—Hardness-time curves for alloy No. 56 quenched from 700°C, cold rolled, and aged at 250°C.

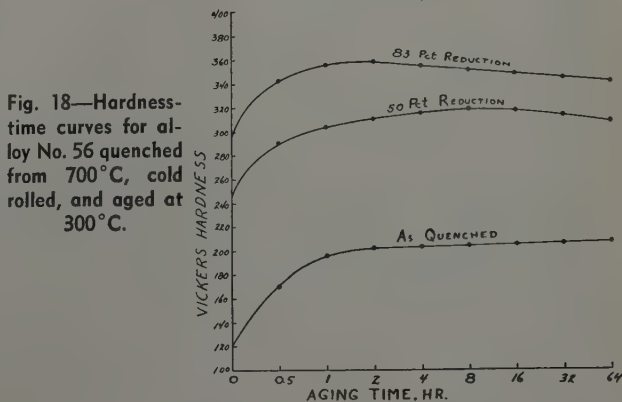


Fig. 18—Hardness-time curves for alloy No. 56 quenched from 700°C, cold rolled, and aged at 300°C.

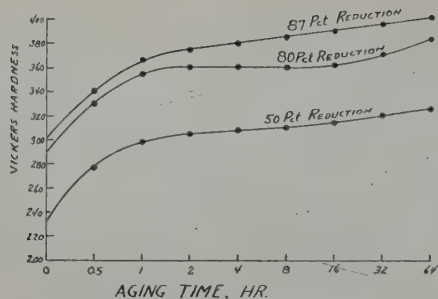


Fig. 19 (left) — Hardness-time curves for alloy No. 50 quenched from 700°C, cold rolled, and aged at 250°C.

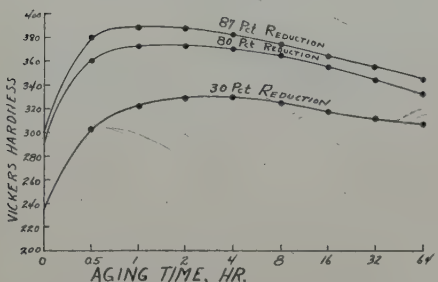


Fig. 20 (lower left) — Hardness-time curves for alloy No. 50 quenched from 700°C, cold rolled, and aged at 300°C.

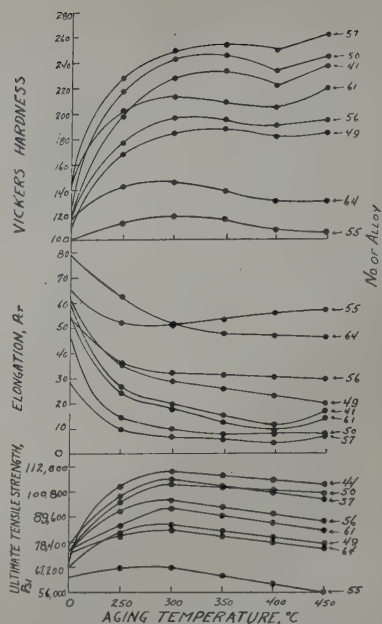


Fig. 21 (right) — Effect of aging temperature on the hardness, tensile strength, and elongation of rolled alloys.

to 20 show the hardness-time curves for two selected alloys solution treated and subjected to varying degrees of cold working followed by aging at 250° or 300°C. These alloys showed an increase in hardness of about 170 as a result of heavy cold working and on aging at 250°C showed a further rapid increase in hardness during the first hour followed by a slower progressive hardening which continued up to 64 hr without any sign of diminishing.

Table IV compares the maximum hardness values obtained for Cu-Sn-Be alloys with the hardness of commercial Cu-Be alloy containing 2.25 pct Be. It is apparent that although the hardness of the ternary alloys when aged from the solution-treated condition does not approach that of the binary Cu-Be alloy, the hardness of the ternary alloys can, if their beryllium content approaches 0.75 pct, be made equal to that of the binary alloy by a combination of cold work and precipitation heat treatment.

Where composition permits a direct comparison to be made, it is noteworthy that the initial and final hardness figures obtained in this work are considerably higher than the corresponding figures reported by Masing and Dahl.

The effects of heat treatment on a few as-cast alloys were examined and were found to be much the same as in the case of the rolled alloys, but the cast alloys gave somewhat lower initial and final hardness figures. The maximum hardness developed at a given temperature was reached in about the same time for both cast and rolled materials. Those alloys which failed to roll satisfactorily, owing to the high proportion of second phase present therein, all

reached high hardness values on heat treatment in the as-cast condition.

**Effect of Aging on Tensile Strength and Elongation:** Tensile tests were carried out on flat specimens 0.1 in. thick having a gage length of 2 in. Specimens were tested after solution treatment at 700°C followed by aging for 1 hr at 250°, 300°, 350°, 400°, and 450°C, respectively. The results obtained are shown in Fig. 21, which also includes comparison curves showing the effect of aging temperature on hardness. For single-phase alloys there is a reasonable correspondence between the effects of aging on hardness and on tensile properties. Perhaps the only significant divergence between the two properties is the lack of any marked increase in ductility in those cases where an increase in aging temperature has led to a fall in hardness. The best tensile properties were revealed by alloy No. 41 (8 pct Sn, 0.75 pct Be, nominal) which, after aging at 300°C, gave a tensile strength of 110,000 psi and an elongation of 23 pct. A similar tensile strength can be induced in high tin-binary bronze by cold working, but the accompanying elongation is much lower than that for the ternary alloy.

**Effect of Aging on Electrical Resistivity:** Resistivity-aging time curves are given in Figs. 22 to 25. There is little correlation between the effect of heat treatment on electrical resistivity and its effect on hardness. On aging at 250° and at 300°C the electrical resistivity of all of the alloys rises slightly at first and then falls continuously. On aging at higher temperatures there is a continuous fall in resistivity. An increase in electrical resistivity frequently occurs during the early stages of precipitation hardening, and the maxima in the hardness and electrical resistivity curves do not necessarily coincide. The maximum resistivity was developed in these alloys before precipitation could be detected under the microscope; this is usual in precipitation hardening.

**Effect of Aging on Microstructure:** After annealing and quenching, alloys outside the  $\alpha$  phase boundary at 700°C were duplex in structure, the second phase being retained  $\beta$ ; the presence of beryllium aids the retention of  $\beta$ .

The metallographic changes during aging were closely followed for alloys containing 10 pct Sn and 0.75 pct Be and those containing 11 pct Sn and 0.5 pct Be (nominal compositions). At all aging tem-

Table IV. Comparative Hardness Values for Cu-Sn-Be and Cu-Be Alloys

| Alloy                                   | Vickers Hardness Number |             |              |                                 |
|-----------------------------------------|-------------------------|-------------|--------------|---------------------------------|
|                                         | Annealed                | Cold Rolled | Heat Treated | Heat Treated after Cold Rolling |
| Commercial Cu-Be (2.5% Be) <sup>a</sup> | 80-100                  | 215-240     | 375          | 390                             |
| 9% Sn, 0.75% Be, Bal. Cu                | 130                     | 290-300     | 260          | 402                             |
| 10% Sn, 0.5% Be, Bal. Cu                | 120                     | 290         | 210          | 375                             |
| 13.5% Sn, 0.25% Be, Bal. Cu             | 135                     | 280         | 190          | 346                             |
| 10% Sn, 0.2% Be, Bal. Cu                | 100                     | 260         | 160          | 298                             |



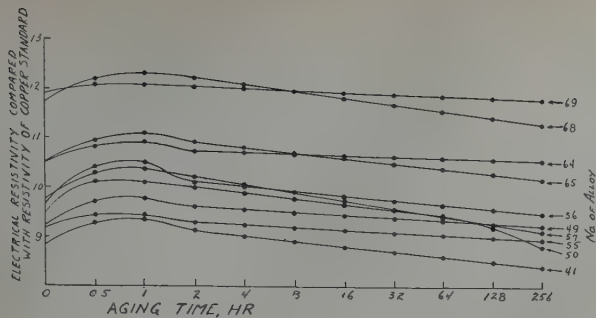


Fig. 22—Electrical resistivity-time curves for rolled specimens annealed at 700°C, water quenched, and aged at 250°C.

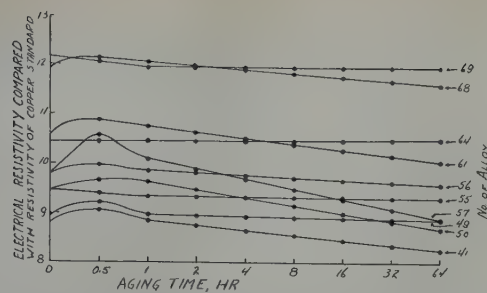


Fig. 23—Electrical resistivity-time curves for rolled specimens annealed at 700°C, water quenched, and aged at 300°C.

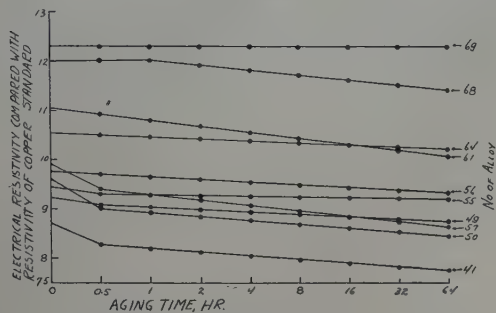


Fig. 24—Electrical resistivity-time curves for rolled specimens annealed at 700°C, water quenched, and aged at 350°C.

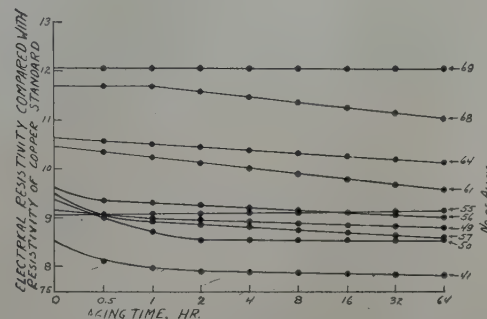


Fig. 25—Electrical resistivity-time curves for rolled specimens annealed at 700°C, water quenched, and aged at 400°C.

temperatures the  $\beta$  phase commences to decompose in the first 30 min. According to the equilibrium diagram, the  $\beta$  phase should be converted to  $\alpha + \delta$  above 350°C and to  $\alpha + \epsilon$  below 350°C; generally speaking, it is impossible to resolve the precipitated individual phases under the microscope. Precipitation occurs in the  $\alpha$  phase of all of the alloys examined and takes place in three stages. In the first stage there is a thickening of the grain boundaries leading to a definite precipitate on further aging. In the next stage martensitic markings develop within the  $\alpha$  grains and increase in intensity as aging proceeds. The third stage, which at 400°C is reached after aging for 4 to 8 hr, corresponds to the disappearance of the martensitic markings and the appearance of precipitated particles within the  $\alpha$  grains, Fig. 26.

Grain boundary precipitation is most marked in alloys that are originally duplex in structure. Precipitation commences from the  $\beta$  areas and the precipitated phase ultimately forms a continuous network surrounding the  $\alpha$  grains, Fig. 27. The presence of this intergranular network is thought to account

for the lower tensile strength of high tin as compared with that of lower tin alloys containing a high percentage of beryllium, see Fig. 21. At higher aging temperatures there is a tendency for the grain-boundary precipitate to ball up and form a discontinuous chain of particles, Fig. 28.

In alloys that are three phase after aging it is impossible to distinguish the two separate phases precipitating in the  $\alpha$  as the structures are so complex, Fig. 29. In these alloys the structure probably consists of an intimate mixture of fine particles of  $\beta'$  CuBe and  $\delta$  or  $\epsilon$  embedded in a matrix of  $\alpha$ . It is only possible in two-phase alloys to obtain structures that can be correlated with the equilibrium diagram by aging the alloys at high temperatures for a long time. Typical structures obtained in this way are shown in Figs. 30 and 31.

The course of precipitation in the low tin, low beryllium alloys is marked at the outset by a thickening of the  $\alpha$  grain boundaries and the appearance of lines of precipitation along lattice planes within the  $\alpha$  crystals, Fig. 32. On further aging, the lines

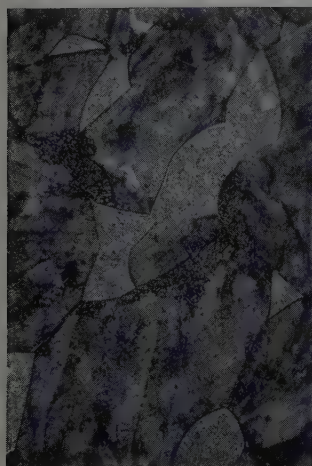


Fig. 26—Structure of alloy No. 57, 10 pct Sn-0.75 pct Be, after aging at 400°C for 8 hr. X500.

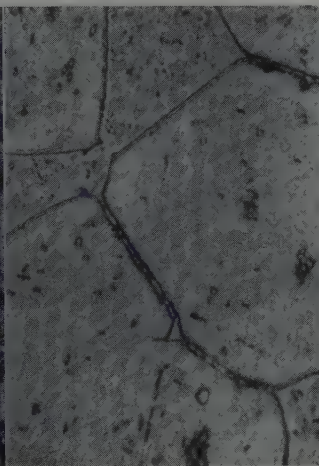


Fig. 27—Structure of alloy No. 68, 13.5 pct Sn-0.25 pct Be, after aging at 350°C for 32 hr. X1000.

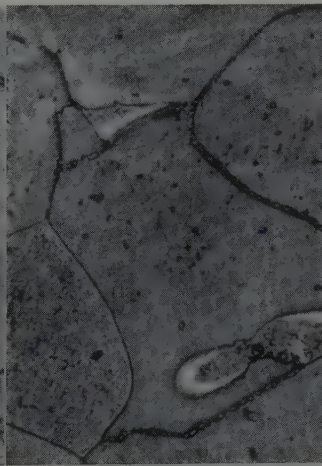


Fig. 28—Structure of alloy No. 61, 11 pct Sn-0.5 pct Be, after aging at 400°C for 1 hr. X1000.



Fig. 29—Structure of alloy No. 57, 10 pct Sn-0.75 pct Be, after aging at 450°C for 128 hr. X500.



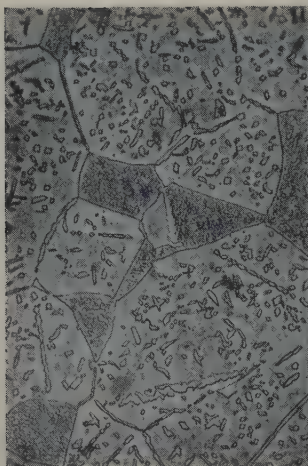


Fig. 30—Structure of alloy No. 68, 13.5 pct Sn-0.25 pct Be, after aging at 400°C for 64 hr. X500.

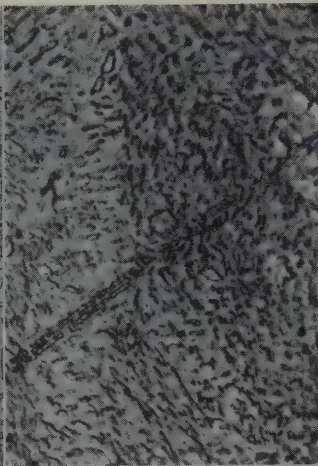


Fig. 31—Structure of alloy No. 41, 8 pct Sn-0.75 pct Be, after aging at 450°C for 256 hr. X2000.

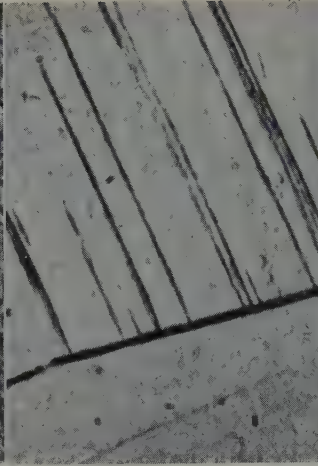


Fig. 32—Structure of alloy No. 27, 5 pct Sn-0.5 pct Be, after aging at 300°C for 4 hr. X2000.



Fig. 33—Structure of alloy No. 5, 2 pct Sn-0.5 pct Be, after aging at 300°C for 8 hr. X500.

of precipitation along the planes within the  $\alpha$  grains become more numerous and it is easy to follow this change of direction at the  $\alpha$  grain boundaries and at twin discontinuities, Fig. 33. On still further prolonging the time of aging, the grain boundaries and lines within the grains become thicker and ultimately it is possible to resolve the latter as particles of the precipitated second phase, Fig. 34.

#### Effect of Aging

The fall in resistivity which occurs on aging Cu-Sn-Be alloys precedes slightly the onset of grain-boundary precipitation. This is in accordance with the hypothesis that maximum lattice strain is reached before visible precipitation occurs. It is somewhat surprising that the appearance of resolvable particles in the  $\alpha$  is not accompanied by a fall in hardness, except for aging at 400° and at 450°C, as in age-hardening systems the hardness generally reaches a maximum before visible precipitation occurs. It is possible that there is some undetected heterogeneity in the  $\alpha$  phase of these ternary alloys and that the softening in certain areas, which theoretically should occur when visible particles form, is offset by hardening in other areas in which precipitation is less advanced. Such heterogeneity might arise through differential stress resulting from non-uniform rolling. However, it is tentatively suggested that in the case of three-phase alloys, which have been annealed at temperatures not exceeding 350°C,

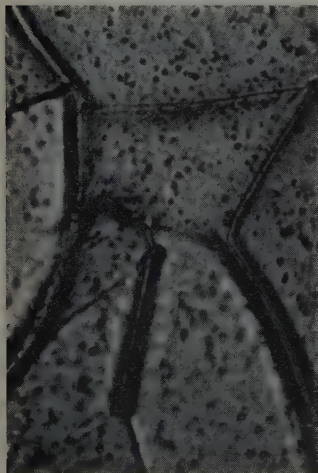


Fig. 34—Structure of alloy No. 27, 5 pct Sn-0.5 pct Be, after aging at 250°C for 32 hr. X2000.

the initial hardening and the first visible precipitation is attributable to precipitation of the  $\beta'$  phase of the Cu-Be system and that subsequent softening is overshadowed by slow, progressive hardening resulting from the sluggish precipitation of the  $\epsilon$  phase.

#### Summary and Conclusions

Isothermal sections of the ternary Cu-Sn-Be system have been determined by microscopic methods for alloys in equilibrium at 700°, 600°, 580°, 500°, 400°, and 300°C and for the composition range 0.25 to 3.0 pct Be and 1.5 to 13.5 pct Sn. The decrease in the limit of  $\alpha$  solid solubility with fall in temperature is found to be more marked than is indicated by the work of previous investigators, particularly at temperatures below 350°C, where the field is restricted by the eutectoid transformation of the Cu-Sn system. The presence of the  $\epsilon$  phase of the Cu-Sn system in specimens that had been annealed at 300°C for 8 weeks was confirmed by X-ray examination.

Alloys containing 0.25 to 0.75 pct Be and 2.0 to 13.5 pct Sn have been shown to possess age-hardening properties. The extent of precipitation hardening obtainable depends primarily on the beryllium content of the alloy. After appropriate aging of rolled and solution-treated material, the maximum hardness is obtained with a nominal composition of 10 pct Sn, 0.75 pct Be. For the same pretreatment, the maximum tensile strength is obtained with a nominal composition of 8 pct Sn, 0.75 pct Be; this alloy can show an ultimate tensile strength of 110,000 psi with an elongation of 23 pct on 2 in. The hardness of the ternary alloys, aged from the solution-treated condition, does not reach that of heat-treated binary Be-Cu alloys with around 2 pct Be, but by cold working solution-treated alloys prior to aging, hardness figures comparable with those exhibited by commercial Cu-Be alloys can be obtained from ternary alloys of suitable composition.

Annealed alloys containing a large amount of second phase tend to crack on cold rolling. These alloys can be heat treated, however, to give high hardness values, a hardness of 260 being attainable for alloys of high tin and high beryllium content.

The constitution changes taking place during precipitation heat treatment have been examined. It is suggested that, on aging three-phase alloys below 350°C, the observed initial hardening is attributable



to precipitation of the  $\beta'$  phase of the Cu-Be system and that the subsequent hardening is explained by slow precipitation of the  $\epsilon$  phase of the Cu-Sn system.

In view of the high cost of beryllium, the fact that approximately the same properties can be obtained in a ternary alloy containing 0.75 pct Be as in a binary alloy containing 2.0 pct Be is noteworthy, and there seems no reason to believe that the cheaper alloy might not function satisfactorily in some of the applications where the binary alloy is now used.

### Acknowledgments

This research was carried out in the laboratories of the Tin Research Institute. The authors are indebted to the International Tin Research and Development Council for permission to publish this paper. Grateful acknowledgment is made for guidance given throughout the course of the work by D. Hanson and G. V. Raynor, of the Department of

Metallurgy, University of Birmingham, England, the former to whom thanks are also due for carrying out the X-ray examination mentioned in the paper, and the latter for helpful advice and criticism.

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### Technical Note

## Lattice Parameter of InSb

by T. S. Liu and E. A. Peretti

**A**LITERATURE survey of the In-Sb system, which was made before a study of the binary diagram was undertaken, revealed that the intermediate phase InSb existed and that its crystal structure is face-centered cubic of the zinc blend type. In 1929 Goldschmidt<sup>1</sup> determined the lattice constant for InSb and obtained a value of 6.452 Å. A more recent value, 6.461 Å was reported by Iandelli<sup>2</sup> in 1941. The purity of the indium used was not very high, however. The indium used by Iandelli contained 2 pct Ge. In view of this fact it was decided to remeasure the lattice parameter using high-purity indium (99.97+ pct In) and spectrographically standardized antimony of the highest purity available (99.91 pct Sb).

Specimens corresponding to the InSb composition were made by carefully weighing the ingredients on an analytical balance and heating them in vacuo in a quartz tube at 700°C. As melting losses were negligible, the alloys were not analyzed chemically, but the intended analysis was taken as being accu-

Table II. Lattice Constant Calculation for Focusing Back-Reflection Pattern Taken at 25°C

| Plane            | $\sin^2\theta$ | $h^2 + k^2 + l^2$ | $\delta^*$ |
|------------------|----------------|-------------------|------------|
| 711 } $\alpha_2$ | 0.976348       | 51                | 5.3        |
| 551 } $\alpha_1$ | 0.972111       | 51                | 6.4        |
| 711 } $\alpha_1$ | 0.972111       | 51                | 6.4        |
| 444 } $\alpha_2$ | 0.922410       | 48                | 17.4       |
| 444 } $\alpha_1$ | 0.917841       | 48                | 18.4       |
| 731 } $\beta$    | 0.913711       | 59                | 19.2       |
| 553 } $\beta$    | 0.874521       | 56                | 27.5       |
| 642 } $\beta$    | 0.820171       | 43                | 38.6       |
| 533 } $\alpha_2$ | 0.816538       | 43                | 39.3       |
| 533 } $\alpha_1$ | 0.816538       | 43                | 39.3       |

Normal Equations

$$184596K\uparrow + 2571.3D = 1097.961$$

$$25171.3K + 4868.44D = 149.5782$$

$$K = 0.00596105 \quad D = -0.00009037 \quad a_0 = 6.4760$$

\*  $\delta = 2\phi \sin^2\theta$ , where  $\phi = 90^\circ - \theta$ .

†  $K = \frac{1}{4}a_0^3$ ,  $\lambda$  is incorporated into the equations.

Values of  $\lambda$  are based on those adopted at the conference of the X-ray Analysis Group of the Institute of Physics, London (1946).<sup>4</sup>

rate. Powder samples were prepared by either filing or crushing of the brittle alloy, followed by screening at 325 mesh. The powders were then annealed at 400°C in evacuated capsules for about an hour.

X-ray photographs were taken with a Debye and a back-reflection focusing camera, using characteristic cobalt  $K_\alpha$  radiation. Lattice parameters were calculated by Cohen's<sup>3</sup> method. The results of a Debye pattern and of a back-reflection pattern at 25°C are given in Tables I and II.

The lattice parameter at 25°C is 6.4760 Å.

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T. S. LIU, Student Associate AIME, is Teaching Fellow and E. A. PERETTI, Member AIME, is Professor of Metallurgy, University of Notre Dame, Notre Dame, Ind.

TN 87E. Manuscript, May 18, 1951.

Table I. Debye Pattern of InSb\*

| $\theta$ | $\sin \theta$ | $d$    | Observed Intensity | hkl              | $\lambda$ |
|----------|---------------|--------|--------------------|------------------|-----------|
| 81.18    | 0.9881        | 0.9054 | m                  | 711 } $\alpha_2$ |           |
|          |               |        |                    | 551 } $\alpha_1$ |           |
| 80.50    | 0.9863        | 0.9050 | vs                 | 711 } $\alpha_1$ |           |
|          |               |        |                    | 551 } $\alpha_1$ |           |
| 73.55    | 0.9590        | 0.9328 | w                  | 444 } $\alpha_2$ |           |
| 73.23    | 0.9574        | 0.9324 | w                  | 444 } $\alpha_1$ |           |
| 69.43    | 0.9362        | 0.8638 | w                  | 642 } $\beta$    |           |
| 65.33    | 0.9086        | 0.9846 | vw                 | 533 } $\alpha_2$ |           |
| 65.10    | 0.9070        | 0.9842 | m                  | 533 } $\alpha_1$ |           |
| 61.23    | 0.8765        | 1.021  | vw                 | 620 } $\alpha_2$ |           |
| 61.05    | 0.8750        | 1.020  | m                  | 620 } $\alpha_1$ |           |
| 55.08    | 0.8200        | 1.089  | s                  | 531 } $\alpha$   |           |
| 51.68    | 0.7846        | 1.138  | vw                 | 440 } $\alpha$   |           |
| 48.13    | 0.7446        | 1.086  | w                  | 531 } $\beta$    |           |
|          |               |        |                    | 333 } $\alpha$   |           |
| 46.23    | 0.7221        | 1.236  | m                  | 511 } $\alpha$   |           |
| 42.90    | 0.6807        | 1.311  | s                  | 422 } $\alpha$   |           |
| 37.38    | 0.6070        | 1.471  | m                  | 331 } $\alpha$   |           |
| 33.93    | 0.5581        | 1.599  | w                  | 400 } $\alpha$   |           |
| 27.63    | 0.4637        | 1.925  | s                  | 311 } $\alpha$   |           |
| 25.08    | 0.4238        | 1.918  | vw                 | 311 } $\beta$    |           |
| 23.40    | 0.3971        | 2.248  | vs                 | 220 } $\alpha$   |           |
| 21.18    | 0.3612        | 2.239  | vw                 | 220 } $\beta$    |           |
| 14.28    | 0.2464        | 3.623  | vw                 | 111 } $\alpha$   |           |

\* Cobalt radiation with iron filter.

s, strong; m, medium; w, weak; vw, very weak.

# Creep Behavior of Zinc Modified by Copper in the Surface Layer

by Milton R. Pickus and Earl R. Parker

THE modern theories of creep<sup>1-4</sup> in general have been based upon the concept of generation and migration of dislocations, with the generation process normally assumed to be rate controlling. The theories are generally deficient in that they fail to take into account many factors that are known to influence creep. The influence of the state of the surface of the test specimen has been almost completely overlooked; yet the present report shows that the nature of the surface may, in certain cases, govern the creep characteristics of a specimen.

In the period since Taylor<sup>5</sup> applied the concept of dislocations to a study of metals, a school of thought has developed that closely relates the plastic deformation of metals to the generation and migration of dislocations through the crystal lattice. It might be expected that the thermal energy required for the generation of a dislocation would be different from that for migration of the dislocation through the lattice. Furthermore, the activation energy for generation would be expected to vary for different parts of the solid metal. It has been predicted that dislocations would be generated most easily at external surfaces, but could also be activated at certain internal surfaces such as grain or phase boundaries. Within the body of the metal a range of values for the activation energy might be expected because of different degrees of disorder at such regions as grain boundaries, impurities, and second-phase particles. The particular value of the activation energy that was rate determining could then depend on the specific conditions of a test. If, for example, the surface atoms were by some means constrained, the generation of dislocations in the body of the metal might become the important factor. On the other hand, other conditions may favor generation at the surface. It is possible then that the creep behavior may not be completely determined by the inherent properties of the metal. Even the environment in which a test is carried out could have a significant effect. In fact it is conceivable that in order to obtain the maximum creep resistance from a given alloy, the surface atoms must be so constrained that the activation energy for generating dislocations on the surface is at least equal to that required for generation in the body of the metal. On the basis of such considerations, and in view of the limited number of publications discussing this subject, it seemed that an investigation of the influence of the state of the surface on creep might yield information of both theoretical and engineering interest.

Experiments on single crystals, demonstrating a variation in the mechanical properties due to alterations in the surface layer, have been reported by several investigators.<sup>6-13</sup> The results of these experiments have been briefly summarized;<sup>14</sup> consequently, the earlier work will not be reviewed here.

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As an example of these findings the observations of Cottrell and Gibbons may be cited. They reported the critical shear stress of a lightly oxidized cadmium single crystal is greater by a factor of  $2\frac{1}{2}$  than a specimen with a clean surface.

## Materials and Methods

Single crystals  $\frac{1}{2}$  in. in diam and 8 in. long were prepared from Horse Head Special zinc, melted under an atmosphere of helium in a large pyrex test tube, and drawn up into a long  $\frac{1}{2}$  in. diam pyrex tube by means of a vacuum pump. The cast zinc rods thus produced were cut into convenient lengths and sealed in evacuated pyrex tubes. Single crystals were grown by gradual solidification of the remelted rods. Cleaving the ends of the single crystal specimens chilled by liquid nitrogen proved a simple method for determining orientations from the exposed basal plane from the markings left on the cleaved surface that gave the slip directions with sufficient accuracy for the experimental work. The specimens chosen for the experiments were those having the angle between the basal plane and the specimen axis within the range of  $15^\circ$  to  $65^\circ$ .

Since zinc single crystals are quite delicate, it was necessary to devise an appropriate method of gripping the specimens in order to suspend them in the furnace and apply the load. Stainless steel collars were prepared having an inside taper, the smaller end of the taper being of such a size that the specimen could just pass through freely. The tapered hole did not extend the full length of the collar; a sufficient thickness of metal remained so that a hook could be attached to provide a means of applying the load and suspending the specimen. One of the collars was slipped over the upper end of a specimen which was supported vertically in a steel jig. The collar was then heated electrically until the end of the crystal melted and filled the collar with molten zinc. At this point the application of heat was discontinued, whereupon the molten zinc quickly solidified, due to the chilling effect of the jig. The specimen was then inverted and the second collar applied in a similar manner. The jig served several purposes: limiting the length of specimen that was melted, providing excellent alignment of the collars with respect to the specimen axis, and protecting the specimen from mechanical damage.

Once the specimen was suspended in the furnace and loaded, it was desired to accomplish the surface treatment with a minimum of disturbance of the specimen. Around the specimen was a long pyrex tube, the upper portion of which was approximately 1 in. in diam, and in it was a copper coil of such a diameter to fit snugly against the tube. A specimen, approximately  $\frac{1}{2}$  in. in diam and 4 in. long, was suspended by means of a stainless steel rod so that it hung within the copper coil. The lower portion of the glass tube was approximately  $\frac{1}{4}$  in. in diam, and passing through it was a  $5/32$  in. diam stainless steel rod which hung from the lower specimen collar. This portion of the glass tube and the stainless steel rod extended through the bottom of the furnace. A T-connector, with suitable packing, was attached to the lower end of the stainless rod to provide a water-



tight seal. A yoke, attached to this rod by a gimbal joint, was used to activate a dial gage and from which the load was suspended by a coil spring. Fig. 1 shows the main features of the assembly.

The furnace consisted of an insulated rectangular box with two nichrome heating elements and a small fan so disposed that a uniform temperature over the gage length of the specimen was obtained. Three thermocouples mounted on a dummy specimen, one at each end, and one at the center of the gage length, showed less than  $1^{\circ}\text{C}$  difference in temperature. Three specimens could be tested simultaneously. A pyrex panel mounted in one of the sides made it possible to observe the specimens.

The gage length consisted of the 4 in. length of crystal between the gripping collars. Overall extension was measured by means of a dial gage graduated in divisions corresponding to a plunger travel of 0.0001 in. The range of the gage was 0.4 in.

The method of achieving reproducible surface changes decided upon consisted in applying electrolytically a thin layer of copper. With respect to zinc, copper may be considered a thermally inactive metal in the sense that at  $200^{\circ}\text{C}$ , for example, the kinetic energy of the copper atoms is still far below that required to overcome the bonding energy that holds the copper atoms in their lattice positions, whereas zinc atoms, in view of the relatively low melting point of  $419^{\circ}\text{C}$ , have kinetic energies more nearly commensurate with the magnitude of the energy holding the zinc atoms together. From these considerations, it was supposed that under the influence of stress and temperature, dislocations could be generated much more easily in a surface layer consisting of zinc atoms than in one containing copper atoms, or for the case where dislocations were generated internally, their escape to the surface would be hampered by the layer of copper.

In order to accomplish the desired changes in the surface layer, procedures were required for cleaning the zinc surface prior to the electrodeposition of copper, and for removing the electrodeposited copper while the specimen was in the assembled apparatus. Fortunately it was found that both of these requirements were met by an anodic treatment of the specimen in an electrolyte consisting of a 10 pct aqueous solution of sodium cyanide, the copper coil (Fig. 1) serving as a cathode. During the development of the anodic treatment, an interesting relationship was observed between the applied voltage and current. Several discontinuities were found, the best cleaning being obtained just after the first. The current was not a single valued function of the voltage; the same current could be obtained at several different voltages, depending on which of the discontinuous curves was applicable. Although the values of the current and voltage at the discontinuities depended on the size of the specimen and the temperature, the cleaning procedure proved to be quite simple, since it was necessary only to apply approximately 4 v and watch the ammeter needle. With the cell filled with electrolyte and the electrical connections made, the current slowly rose to a maximum and then dropped sharply. After 10 or 15 sec at the lower current the specimen was found to be cleaned effectively.

If the specimen was to be copper plated, the sodium cyanide solution was drained off, the polarity of the electrodes reversed, and the cell filled with a copper-plating solution. The zinc specimen was plated at a current density of 0.10 amperes per sq

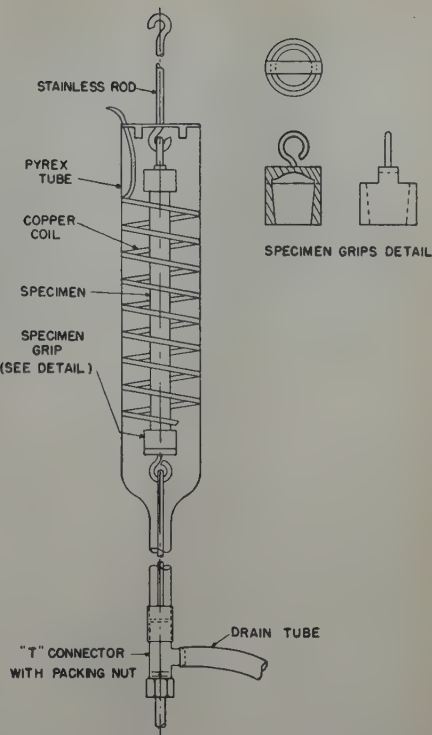


Fig. 1—Specimen assembly.

in. for 90 sec. Both the specimen and electrolyte were at room temperature during the plating. The composition of the plating bath was as follows: Copper cyanide, 22.5 g per liter; sodium cyanide, 33.8; sodium carbonate, 15. The average thickness of the copper layer deposited under these conditions is  $10^{-5}$  in. After plating, or cleaning if that was to be the final step, the cell was rinsed first with water and then with alcohol. Finally the specimen and cell were dried by the passage of a stream of air.

In order to determine the effects of the copper deposit, it was found necessary to employ a single specimen for a complete test involving alternate changes in the surface layer. This procedure had the advantage of reducing the number of variables, although it did require an interruption in the test. Earlier experiments had shown that despite the care employed in the preparation of the single crystals, they nevertheless differed from one another in that the same creep rates for different orientations could not be obtained by adjusting the load to provide the same shear stress in the direction of slip. For one thing the extension was by no means uniform over the 4 in. gage length. In this respect there was a variation from one specimen to another. In an extreme case the entire deformation was localized in a small portion of the specimen, which had the appearance of two substantially undeformed portions markedly offset from each other over the width of a narrow slip band. This of course means that measuring the overall extension of the 4 in. specimen can give only a fictitious strain rate, since the true gage length is indeterminate. However, the measurement of the overall extension served as a convenient means of observing changes in a particular specimen. A few of the specimens subjected to elevated temperature creep tests are shown in Fig. 2. It should also be mentioned in this connection that the loading of the specimens to obtain the desired creep rate proved to be quite a problem. In many cases only a small increment of load beyond that producing a very slow rate of secondary creep resulted in the sudden onset of the third stage, with

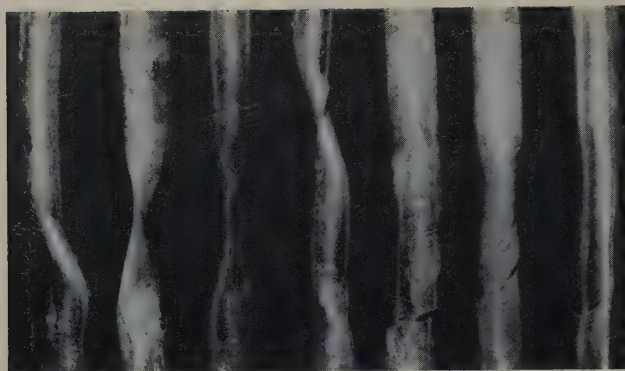


Fig. 2—Examples of unplated zinc single crystals tested in creep at elevated temperatures.

large extensions occurring in a relatively short time. In some instances this increment of load was supported by the specimen for several hours, the creep progressing at a slow steady rate; then the creep rate would rise sharply, producing such excessive extension the particular test had to be abandoned.

After the specimen assemblies were suspended in the furnace, the specimens were cleaned anodically in the sodium cyanide solution and then rinsed and dried. The furnace then was heated to a higher temperature than was to be used for the tests, and a period allowed for temperature stabilization with the object of minimizing any changes in the state of the specimens due to heating at the test temperature. The furnace was cooled and brought to equilibrium at the test temperature before the load was applied. After the secondary creep rate was determined, the furnace was cooled to room temperature, with the specimens still under load. They were again cleaned anodically in the sodium cyanide solution, after which they were copper plated in the manner already described. The furnace was reheated to the test temperature and the secondary creep rate for the copper-plated condition determined. As already mentioned, the copper layer was effectively removed by the anodic cleaning procedure. Thus several cycles of creep for each condition of the specimen surface could be observed.

This procedure was adopted after several unsuccessful modifications. It was thought that for tests at temperatures near 100°C hot solutions could be employed, thus eliminating the necessity for interrupting the test by cooling down the furnace. However, the anodic treatment in sodium cyanide solution was not controllable in hot solutions.

On the other hand, if the furnace was maintained at the test temperature, and the specimens momentarily chilled by filling the cells with cool liquid, an effect of the cooling on the creep rate was invariably observed. This effect was analogous to that obtained by adding an increment to the load. The

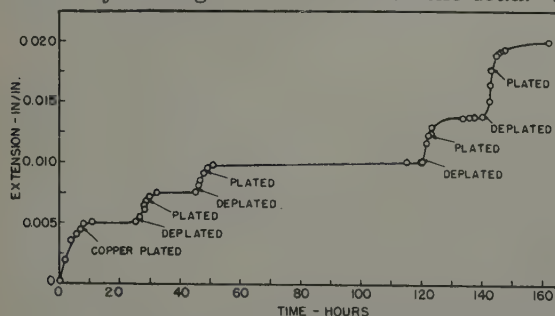


Fig. 3—Change in creep rate of a zinc single crystal produced by a thin copper plate. Test temperature, 100°C. Resolved shear stress, 31.5 psi.

creep rate increased rather sharply and the effect persisted for several hours.

Several tests were performed wherein during a period of steady creep no change was made other than to cool the furnace to room temperature, and then reheat it to the test temperature. In all cases the creep rate was unchanged by the slow cooling and heating cycle. It appeared, therefore, that in order for there to be an effect on the creep rate due to cooling the specimen, a temperature differential must be set up between the surface and interior of the specimen. The fact that no noticeable effect was introduced by gradual cooling was regarded as justification for the test procedure that was adopted.

In this manner the effect of copper in the surface layer on the secondary creep rate was studied at constant temperature and constant load. This was done for polycrystalline zinc and for single crystals. The temperature dependence at constant load of the secondary creep rate was also determined for both forms of zinc with and without the presence of an electrolytically deposited layer of copper.

The polycrystalline specimens were in the form of

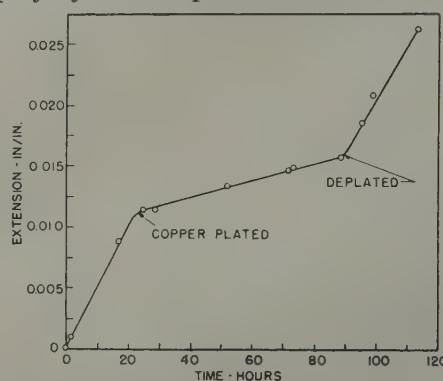


Fig. 4—Change in creep rate of a zinc single crystal produced by a thin copper plate. Test temperature, 200°C. Resolved shear stress, 26.5 psi.

cast rods of chemically pure zinc. While the grain size of these specimens was somewhat coarse, a cross-section contained many grains so that a comparison between single crystal and polycrystalline zinc could be obtained. The polycrystalline specimens were 5½ in. long and ¼ in. in diam, with a 2 in. reduced section of 0.187 in. diam which served as the gage length.

### Experimental Results

In the course of the experimental work a large number of single crystals in a considerable range of orientations were tested. The results in all cases followed the same general pattern. The creep rate was sharply decreased by the presence of the thin copper layer. When the copper was removed, the creep rate increased to the value obtained for the unplated specimen. The effect of the copper was large, amounting in some cases to essentially a complete cessation of flow. In an extreme case when a test was carried to a point where the cross-sectional area was noticeably diminishing, the application of the copper deposit arrested the acceleration of creep rate.

The results of typical tests are shown graphically in Figs. 3 and 4. In Fig. 3 is recorded a test at 100°C showing the effect of a series of plating and deplating cycles. Even though necking had begun in the latter stages of the test, the effect of the copper was still definite. Fig. 4 shows the results of a similar test at 200°C.

Numerous tests on the polycrystalline specimens



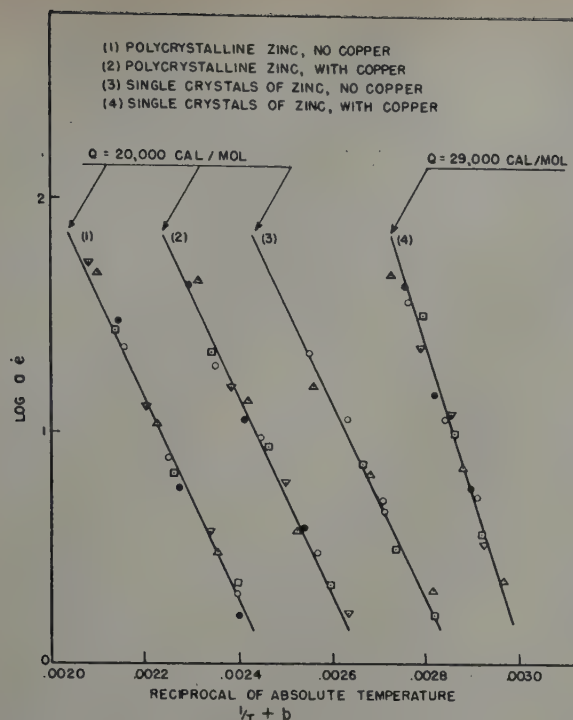


Fig. 5—Composite plot of data from 18 tests designed to establish the temperature dependence of creep for polycrystalline and single crystal zinc both with and without copper on the surface.

Creep rate designated as  $\dot{\epsilon}$ . The constants  $a$  and  $b$  were selected to shift the curves parallel to their original positions for ease of comparison. All the experiments were in the temperature range of 200° to 325°C.

show conclusively that the presence of a thin layer of copper has no effect on the creep behavior of polycrystalline zinc. While particular experiments might indicate an effect of small magnitude, the effect is so small as to be within the scatter of results obtained over many experiments.

The secondary creep rates for zinc in four different conditions were determined in the temperature range 200° to 375°C. The four conditions comprised single crystal and polycrystalline zinc, both with and without the presence of copper in the surface layer. The test procedure consisted of determining for each specimen the creep rates at three different temperatures. After the creep rates were determined for each of the three temperatures, the test at the first temperature was repeated as a check that no appreciable change in the state of the specimen had occurred. The data were plotted with the logarithm of the creep rate as ordinate and the reciprocal of the absolute temperature as abscissa. It is characteristic of the second stage of creep that the creep rate changes very little for relatively large strains. The approximately steady secondary creep rate is known to vary with temperature in close accord with the expression:

$$\text{Creep rate} = A e^{-Q/RT}$$

where  $A$  is a constant;  $e$ , the natural logarithm base;  $Q$ , a quantity known as the activation energy;  $R$ , the gas constant; and  $T$ , the absolute temperature.

The results of these tests have been summarized in the composite plot shown in Fig. 5. In this series of experiments, the objective was to determine the effect of the copper plate on the temperature dependence of creep. Both single and polycrystalline specimens were tested. The lines drawn through the points represent a graphical averaging of the data obtained from numerous tests. The lines have been separated for clarity by shifting the ordinates to a different position on the graph for each type of

specimen. However, the range of temperatures and creep rates were approximately the same for all tests (see Figs. 3 and 4 for typical creep rates), so that a direct comparison of temperature dependence could be made. Individual tests are distinguished by the use of different symbols. The values of  $Q$  were determined from the slopes of these four lines. It will be noted that the same value of  $Q$  was obtained for single crystals without copper, and for polycrystalline zinc with and without copper in the surface layer. Of the four conditions studied only the copper-plated single crystals showed an appreciably different temperature dependence.

An observation was made in regard to the copper-plated single crystals that is of considerable interest. It was found that if, after the creep rate had been determined at three successively higher temperatures, the temperature was lowered for a period of 15 hr, or so, to a point where creep progressed very slowly, reheating the specimen to the original three test temperatures gave appreciably lower creep rates. The log (creep-rate) vs.  $1/T$  plot was a straight line parallel to the line obtained originally, but displaced in the direction of lower creep rates. This effect was observed consistently and is illustrated for a particular test in Fig. 6. The magnitude of the effect may be appreciated by comparing points (1) and (4) which show corresponding creep rates obtained at 275°C before and after the low temperature treatment. This strengthening effect may be due to the clustering of solute atoms around dislocations which reduces their mobility.

### Discussion of Results

Since a relatively thin deposit of copper had such a pronounced effect on the creep behavior of zinc single crystals, it becomes important to consider in what manner the copper exerts its influence. Before discussing the various mechanisms that might account for these results, it is necessary to take into account an additional experimental observation. In all the tests that were performed, diffusion between zinc and copper occurred. The diffusion was quite

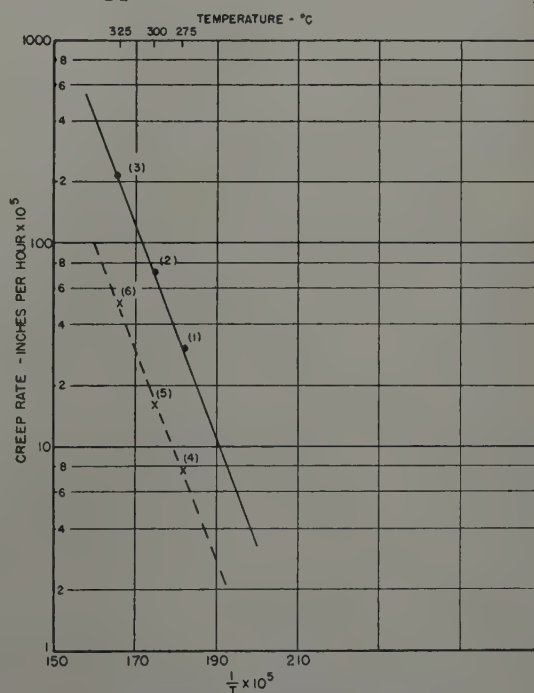


Fig. 6—Temperature dependence of copper-plated zinc single crystal showing effect of a period of very slow creep.

After determining points 1, 2, and 3, specimen was cooled under load to 250°C and held at this temperature for 15 hr. Then points 4, 5, and 6 were determined.

rapid; before the specimens attained the test temperature, little visible evidence of the copper deposit remained. However, that the copper remained in the extreme surface layer of the specimen was indicated by the fact that the slight amount of material removed by the anodic treatment in sodium cyanide solution caused the creep rate to increase to the value obtained before plating with copper. It has already been mentioned that during the anodic treatment of the zinc specimens a discontinuous relationship was observed between the applied voltage and the current. When copper was present these discontinuities did not occur. As soon as a surface of essentially pure zinc was exposed, the discontinuities reappeared. This served as a convenient control of the cleaning procedure. Any attempt, therefore, to rationalize the results must take into account the fact that the surface layer consists of a Cu-Zn alloy.

The question arises as to whether the effect of the copper on the creep of zinc single crystals is simply a mechanical one; that is to say, the Cu-Zn surface layer produces a strengthening effect analogous to increasing the specimen diameter by an equivalent thickness of zinc. Stress analyses indicate that this is unlikely and furthermore, if this were the case, no difference in the temperature dependence would be expected between the plated and unplated crystals. The fact that a difference was found suggests that there is a fundamental difference in the creep process for the two surface conditions.

The possibility of developing stresses in the surface layer as a consequence of the application of the copper must also be considered. Such stresses could arise from at least two sources. The existence of stresses in electrodeposited metal is common knowledge. Such stresses may be either tensile or compressive in nature, depending on the metal being deposited and the conditions of electrodeposition. Another source of surface stress lies in the fact that diffusion occurs between the copper and zinc. This causes a change in the lattice parameter at the surface and thus produces a potential localized stress field. While such stresses might conceivably affect the creep rate at a given temperature, it is difficult to see how they could account for a change in the temperature dependence, particularly since the temperature coefficient for unplated zinc was found to be rather insensitive to changes in the stress level. Moreover, the fact that the tests were conducted at elevated temperatures would tend to limit the magnitude of the localized stresses.

Another pertinent question is why the copper deposit had no effect on the creep behavior of polycrystalline zinc. If it is assumed that the generation of dislocations, rather than their migration through the lattice, is rate determining, a possible explanation for this difference in behavior can be offered. It is a reasonable assumption that dislocations can be more easily generated at a surface than in a volume of perfect crystal. In a single crystal the only surface is the external one (neglecting domain boundaries); whereas in a polycrystalline specimen there is a network of internal surfaces as well. Since, in the latter case the external surface is only a small percentage of the total available surface area, a polycrystalline specimen would not be expected to be sensitive to alterations in the external surface. However, evidence has been obtained that indicates such a conclusion may be incorrect. Some tests were performed on polycrystalline "A" nickel, the results of which have been published.<sup>14</sup> A com-

parison was made of the creep behavior of "A" nickel in different environments and surface conditions. It was found that resistance to high temperature creep was much greater in air than in either purified hydrogen or nitrogen. The experiments with "A" nickel were therefore interesting with respect to the strengthening effects that have been reported for single crystals due to an oxide film. Similar results recently have been obtained for copper. It now appears that oxide films are also significant for polycrystalline metals.

In the case of the zinc single crystals the possibility of a volume, rather than a surface effect, would appear to be ruled out by the observation that the removal of a small amount of surface material from a copper-plated specimen caused the creep rate to increase to the value obtained for unplated specimens.

The results presented herein do not constitute a proof that dislocations originate at the surface of single metal crystals during a creep test. It may well be that dislocations are generated internally as postulated by Frank and Reed<sup>15</sup> and that their egress is blocked by the surface layer. At the present time it is not possible to locate the origin of the dislocations. However, additional experiments are now under way which may prove sufficiently critical to establish whether dislocations are generated within the volume of a crystal or at external or grain surfaces.

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# Equilibrium Relations in Magnesium-Aluminum-Manganese Alloys

by Benny J. Nelson

AS a part of the fundamental research program of Aluminum Research Laboratories, some data were obtained on the ternary system Mg-Al-Mn. As very little information on the magnesium corner of this diagram has heretofore been published, it seems desirable to make available the values found for the liquidus and solidus surfaces of this system.

## Procedure

The settling procedure was used for the determination of the liquidus compositions. Metallographic examination of quenched samples, and stress-rupture upon incipient melting, were used for the solidus determinations.

The settling procedure has been described in a previous paper.<sup>1</sup> Briefly, this method involved saturating the alloy with manganese at a temperature substantially above that at which the solubility was to be determined, then cooling the melt to the latter temperature, and holding it at that temperature for a substantial period of time. Samples for analysis were carefully ladled from the upper portion of the melt at hourly intervals during the holding period. After the ladling of each sample, the melt was stirred to redistribute some of the manganese that had already settled, because it appeared that when the latter particles of manganese again settled, they aided in carrying down more of the manganese and thus hastened the attainment of equilibrium.

The melts were prepared and held in a No. 8 Tercod crucible holding approximately 4 lb of metal. The manganese was added either in the form of a prealloyed ingot (Dow M) containing about 1.5 pct Mn or by the use of a flux (Dow 250) containing manganese chloride. In calculating the flux additions, it was assumed that the manganese introduced would be equal to 22 pct of the total weight of the flux. Temperatures were measured with an iron-constantan thermocouple enclosed in a seamless steel tube, the lower end of which was welded shut. This protection tube also served as a stirring rod. The samples ladled from the upper portions of the melts at the various intervals were analyzed for aluminum, manganese, and iron.

When making the alloys which were to be used for the determination of the solidus, 2½ in. diam tilt mold ingots were cast, scalped to 2.0 in. in diam, and extruded into ½ in. diam wire. The principal impurities in the melts for this investigation were iron and silicon; their total not exceeding 0.03 pct.

Portions of the wire, approximately 2 in. in length, were enclosed in stainless steel capsules for protection from the atmosphere. Bundles of these capsules, with a dummy capsule containing an iron-constantan thermocouple, were heated inside a large steel block (acting as a heat reservoir) in a closed circulating-air type electric furnace. At ap-

propriate times, the capsules were removed and quenched in water. The wires were examined metallographically to determine the temperature of initial melting.

Short times at temperature were used at the beginning for wire specimens of all alloys to obtain quickly the approximate temperatures at which melting could be first observed. When approximate solidus temperatures had thus been determined, equilibrium heating was attempted. This equilibrium heating consisted of an 8 or 16 hr period at a temperature, about 50°F below the lowest temperature at which melting occurred when short heating cycles were used, followed by further heating for 1 hr periods at consecutive 10° higher temperatures.

The theory for the method of stress-rupture at incipient melting has been well covered<sup>2</sup> and its limitations are recognized. Thus, if the interfacial tensions are such that the first minute quantity of liquid is "bunched up" at the grain boundary junctions instead of spreading out along the grain boundaries,<sup>3</sup> temperatures higher than the solidus are required before melting will be manifested by rupture of the specimen. This point will be elaborated later.

Specimens of the wires with a reduced section (approximately 1/16 in. diam) were suspended vertically in a tubular furnace. The setup used is shown in Fig. 1. The clamp holding the specimen was made from alumel thermocouple wire and the thermocouple was thus completed across the specimen by attaching a chromel wire to its lower end. Temperatures were read from a Speedomax recorder used in conjunction with a calibrated thermocouple. The small weight attached to the specimen and a vibrator attached to the furnace tube, to aid in distributing the molten constituent along the grain boundaries, were used to bring about rupture at a temperature closely approximating the solidus. The specimens were heated at a rate of about 5°C per min. The rupture of the specimens was indicated both by sound and by the action of the recorder. An argon atmosphere containing a small amount of SO<sub>2</sub> was used for protection of the specimen. The assembly was taken out of the furnace immediately following rupture and the specimen removed. Some of the broken specimens were examined metallographically and will be referred to later.

## Results and Discussion

Fig. 2 shows a set of typical time-composition curves for liquid samples of the Mg-Al-Mn alloys used for the settling tests. The data as presented

Table I. Limiting Values for Liquid Solubility of Manganese in Mg-Al-Mn Alloys

| Settling<br>Tempera-<br>ture,<br>°F | Nominal<br>0.8% Al |      | Nominal<br>1.6% Al |      | Nominal<br>4.5% Al |      | Nominal<br>7.5% Al |      |
|-------------------------------------|--------------------|------|--------------------|------|--------------------|------|--------------------|------|
|                                     | Al                 | Mn   | Al                 | Mn   | Al                 | Mn   | Al                 | Mn   |
|                                     | Pct                | Pct  | Pct                | Pct  | Pct                | Pct  | Pct                | Pct  |
| 1500                                | 0.57               | 2.66 | 1.63               | 2.05 | 4.62               | 1.70 | 7.56               | 1.43 |
| 1475                                | 0.65               | 2.28 | 1.66               | 1.95 | 4.43               | 1.55 | 7.45               | 1.31 |
| 1450                                | 0.55               | 1.94 | 1.91               | 1.76 | 4.31               | 1.40 | 7.13               | 1.10 |
| 1400                                | 0.86               | 1.75 | 1.53               | 1.54 | 4.17               | 1.18 | 7.31               | 0.98 |
| 1350                                | 0.52               | 1.46 | 1.31               | 1.31 | 4.35               | 0.83 | 7.08               | 0.80 |
| 1300                                | 0.50               | 1.30 | 1.45               | 1.02 | 4.27               | 0.73 | 6.82               | 0.63 |
| 1250                                | 0.58               | 0.90 | 1.55               | 0.76 | 4.05               | 0.56 | 7.02               | 0.40 |
| 1200                                |                    |      | 1.58               | 0.50 |                    |      | 6.99               | 0.32 |

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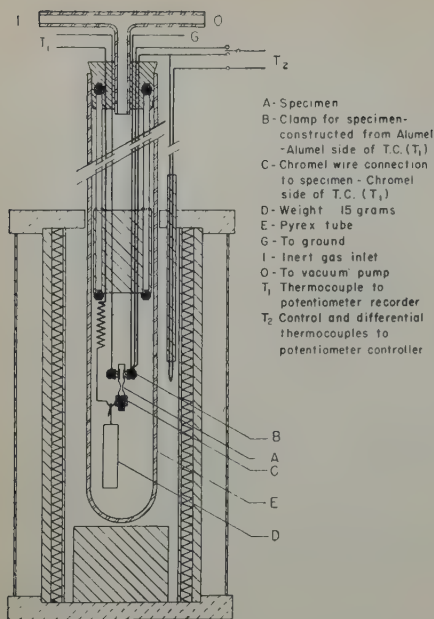


Fig. 1 (left)—Apparatus for determining solidus temperatures in magnesium alloys by the stress-rupture method.

Fig. 2 (right)—Liquid solubility of manganese in Mg-4.5 pct Al alloy as determined by settling tests.

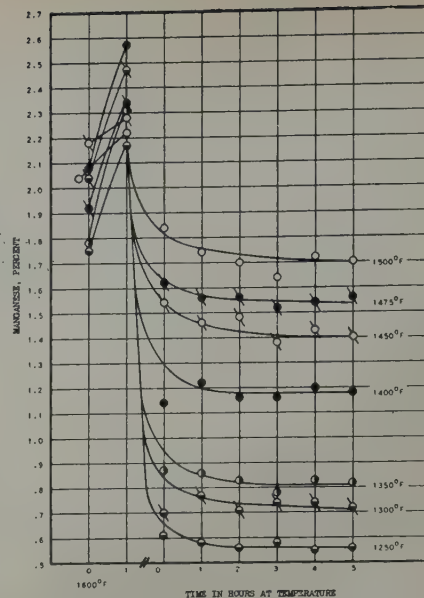
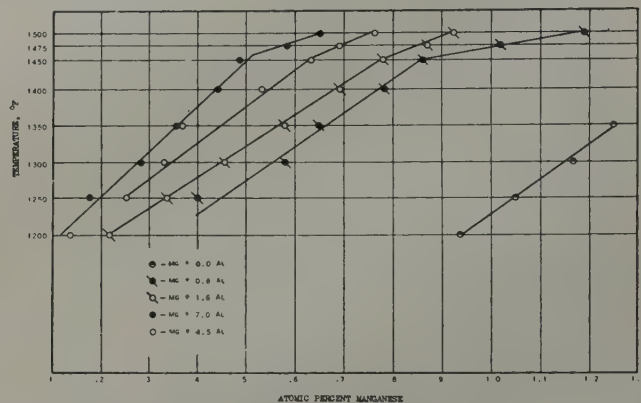


Fig. 3 (lower left)—Liquid solubility of manganese in Mg-Al alloys as determined by limiting values on settling test curves.

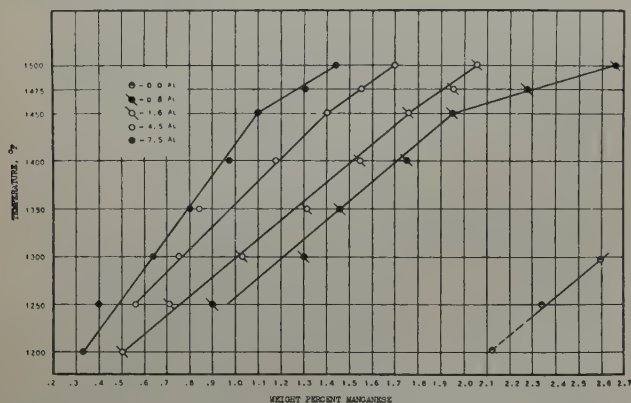
Fig. 4 (lower right)—Liquid solubility of manganese in Mg-Al-Mn alloys plotted as the logarithm of atomic percentage of manganese vs. the reciprocal of absolute temperature.



ture for both aluminum and manganese for the different nominal aluminum content series.

Fig. 3 shows the liquidus curves in weight percentage of manganese for these alloys vs. degrees F, while Fig. 4 shows the solubility of manganese in atomic percentage vs. the reciprocal of the absolute temperature (corresponding degrees F being indicated). The values for zero pct Al are taken from the results of Tiner.<sup>4</sup> The liquidus curves take a decided change in slope in the neighborhood of 1450°F, possibly indicating a peritectic reaction.

As would be expected, the addition of aluminum to the Mg-Mn alloys lowers the solubility of man-



show that, in general, supersaturation is established before the settling period begins. The manganese concentration usually rises during the period in which the melt is held at 1600°F and after the temperature is lowered, falls rather quickly to a limiting value, which is taken as the solubility of manganese in the alloy at the lower temperature. In all cases, solubility curves were determined on the basis of the average manganese contents during the last few hours of settling. It should further be brought out that the aluminum content as given for the curves is the nominal composition; the actual content for each sample varied somewhat from this nominal. Table I gives the "limiting" values at each tempera-

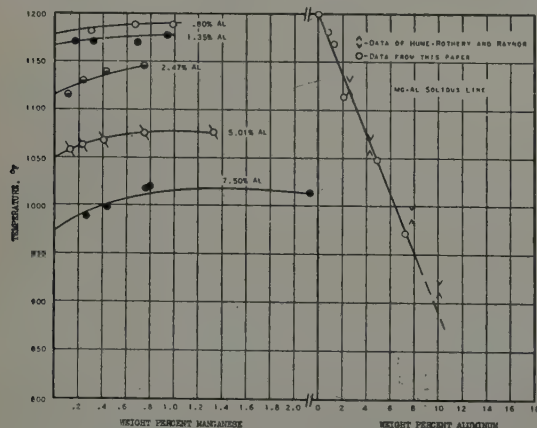


Fig. 5—Solidus temperatures in magnesium base Mg-Al-Mn alloys and the Mg-Al solidus line.

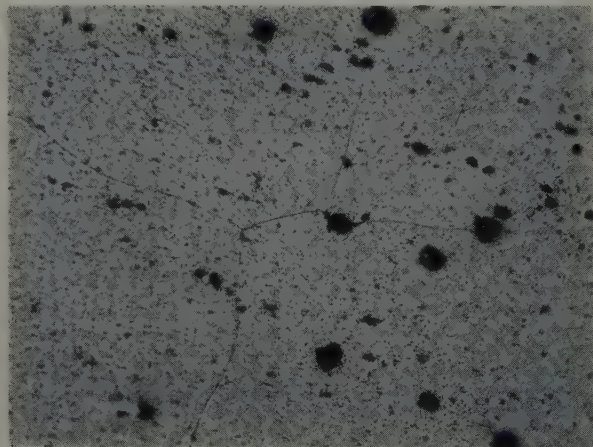


Fig. 6—Microstructure of Mg-7.25 Al-2.11 Mn alloy fractured at 1013°F. Notice narrowness of grain boundaries and the absence of bunching up at the grain junctions. Etched with Keller's etch. X500.



Table II. Solidus Temperatures in Mg-Al-Mn Alloys

| S-No.   | Al % | Mn % | Fe %  | Si %  | Temperature Determined<br>by Metallographic<br>Examination of<br>Quenched Wires |             | No. of<br>Tests | Average<br>Temperature,<br>°F | Standard<br>Deviation,<br>°F |
|---------|------|------|-------|-------|---------------------------------------------------------------------------------|-------------|-----------------|-------------------------------|------------------------------|
|         |      |      |       |       | Non-<br>Equilibrium                                                             | Equilibrium |                 |                               |                              |
| 117654  | 0.81 | 0.31 | 0.028 | <0.01 | *                                                                               | *           | 3               | 1182                          | 1.0                          |
| 117656  | 0.81 | 0.79 | 0.020 | <0.01 | —                                                                               | 1180        | *               | *                             | *                            |
| 117657  | 0.80 | 0.99 | 0.018 | <0.01 | 1180                                                                            | **          | 3               | 1188                          | 0                            |
| 117659  | 0.79 | 0.67 | 0.001 | *     | —                                                                               | 1180        | 4               | 1188                          | 1.8                          |
| 117648  | 1.32 | 0.17 | 0.027 | <0.01 | —                                                                               | 1190        | 3               | 1171                          | 1.8                          |
| 117649  | 1.32 | 0.32 | 0.024 | <0.01 | 1180                                                                            | —           | 3               | 1171                          | 4.8                          |
| 117652  | 1.30 | 0.94 | 0.011 | <0.01 | —                                                                               | 1180        | 3               | 1177                          | 2.9                          |
| 117658  | 1.47 | 0.69 | 0.001 | *     | —                                                                               | 1170        | 3               | 1170                          | 1.0                          |
| 94369-1 | 2.42 | 0.11 | 0.021 | —     | 1106                                                                            | 1120        | 3               | 1117                          | 1.0                          |
| 94369-2 | 2.50 | 0.24 | 0.028 | —     | 1120                                                                            | 1130        | 3               | 1130                          | 2.5                          |
| 94369-3 | 2.53 | 0.43 | 0.027 | —     | 1130                                                                            | 1140        | 3               | 1139                          | 5.2                          |
| 94369-4 | 2.44 | 0.75 | 0.009 | —     | 1120                                                                            | —           | 3               | 1146                          | 2.3                          |
| 94370-1 | 5.09 | 0.15 | 0.029 | —     | 1050                                                                            | 1050        | 7               | 1058                          | 5.1                          |
| 94370-2 | 5.07 | 0.23 | 0.022 | —     | 1060                                                                            | 1070        | 6               | 1063                          | 9.1                          |
| 94370-3 | 5.07 | 0.41 | 0.027 | —     | 1060                                                                            | 1060        | 7               | 1067                          | 7.1                          |
| 94370-4 | 5.09 | 1.33 | 0.025 | —     | 1070                                                                            | 1080        | 3               | 1076                          | 2.3                          |
| 94370-5 | 4.75 | 0.75 | 0.001 | —     | 1070                                                                            | 1080        | 3               | 1076                          | 1.4                          |
| 94371-1 | 7.85 | 0.26 | 0.029 | —     | 990                                                                             | 980         | 4               | 988                           | 3.8                          |
| 94371-2 | 7.81 | 0.44 | 0.020 | —     | 990                                                                             | 990         | 4               | 997                           | 3.8                          |
| 94371-3 | 7.49 | 0.66 | 0.008 | —     | 1000                                                                            | 1000        | *               | *                             | *                            |
| 94371-4 | 7.25 | 2.11 | 0.010 | —     | 1010                                                                            | 1020        | 11              | 1013                          | 13.4                         |
| 94371-5 | 7.28 | 0.76 | 0.001 | —     | 1020                                                                            | 1020        | 8               | 1017                          | 11.4                         |
| 94371-6 | 7.34 | 0.80 | 0.001 | —     | 1020                                                                            | 1030        | 10              | 1020                          | 5.0                          |

\* Not determined.

\*\* Equilibrium conditions not attained.

ganese in the ternary alloy. The striking influence of small amounts of aluminum in decreasing the liquid solubility of manganese in these alloys is readily apparent.

It should be emphasized that the numerical value of atomic percentage of manganese for each point on all of these curves was calculated separately. This was necessary because in all cases there was some change in the aluminum content as the limiting solubility of manganese was reached; the best average for the limiting values of both aluminum and manganese was used as is shown in Table I.

#### Solidus Temperatures in Mg-Al-Mn Alloys

As stated earlier, both metallographic examination and the stress-rupture method were used to determine the solidus temperatures of the Mg-Al-Mn alloy wires.

Table II gives the solidus temperatures of the wires as determined by these two methods. Considering the limitations of each method, the agreement between the results is fairly good, particularly for the alloys of low to medium aluminum content.

Fig. 5 shows the effect of manganese on the solidus temperature as determined by the stress-rupture method; the aluminum values listed for the curves are averages. It is seen that the manganese significantly raises the solidus temperature of Mg-Al alloys. This figure also shows the Mg-Al solidus line when these curves are extrapolated to zero pct Mn, together with the Mg-Al solidus data of Hume-Rothery and Raynor.<sup>5</sup> The agreement between the present data and that of ref. 5 for the solidus is fair.

It was mentioned earlier that the distribution of the liquid phase would have an influence upon the temperature of fracture. The microstructure of one of the specimens from the stress-rupture test is shown in Fig. 6. No tendency for the melted constituent to "bunch up" at the grain boundaries is noted; the film of liquid along the grain boundaries is so thin it is difficult to show in the micrograph.

#### Conclusions

Liquidus and solidus determinations have been made in the ternary system Mg-Al-Mn and these are shown by a series of curves. The following conclusions can be drawn:

1—The solubility of manganese in liquid magnesium is greatly depressed by the addition of a small amount of aluminum, and is further depressed by increasing amounts of aluminum in the alloys.

2—There is a discontinuity in the slope of the liquidus surface in the magnesium corner at about 1450°F.

3—The solidus temperature of alloys in the magnesium corner decreases markedly with increasing aluminum content for alloys having approximately equal manganese contents.

4—The solidus temperature increases substantially with increasing manganese.

#### Acknowledgment

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# Crystal Structure of $\text{UAl}_4$

by Bernard S. Borie, Jr.

THE U-Al binary system has been studied by Kaufmann and Gordon.<sup>1</sup> They have shown that three intermetallic compounds occur in the system:  $\text{UAl}_3$ ,  $\text{UAl}_2$ , and a third compound tentatively identified as  $\text{UAl}_4$ .  $\text{UAl}_3$  is simple cubic,  $a_0 = 4.26\text{\AA}$ . Its unit cell contains one formula weight, and it is isomorphous with  $\text{AuCu}_3$ .  $\text{UAl}_2$  is face-centered cubic,  $a_0 = 7.72\text{\AA}$ , with eight formula weights per unit cell. Rundle and Wilson have shown that it is isomorphous with  $\text{Cu}_2\text{Mg}$ .<sup>2</sup> A Debye-Scherrer pattern of the Al-rich compound indicated a more complex structure than either  $\text{UAl}_2$  or  $\text{UAl}_3$ . The following is a report of an investigation of the crystal structure of this compound and a determination of its stoichiometric formula.

A melt of uranium (99.9 pct pure) and aluminum (99.9 pct pure) was prepared which contained about 25 pct U by weight. It was cooled from  $950^\circ$  to  $650^\circ\text{C}$  at a rate of  $500^\circ$  per hr and then taken from the furnace and air cooled. An X-ray diffraction pattern of the ingot showed only lines of aluminum and the Al-rich compound. Filings from the ingot were reacted with a solution of sodium hydroxide, producing a fine black powder, the diffraction pattern of which showed no traces of aluminum. A comparison of the Debye-Scherrer pattern of our sample with the data published by Kaufmann and Gordon<sup>1</sup> showed that it is identical with the Al-rich phase which they reported.

Single crystals were obtained by cooling the melt more slowly (about  $50^\circ\text{C}$  per hr). After reaction with sodium hydroxide, the crystals appeared as small black needles attached to the ingot surface.

## Cell Size, Space Group, and Uranium Positions

A series of Weissenberg photographs for rotation about two of the crystallographic axes, taken with copper radiation filtered through nickel foil, revealed an orthorhombic cell of dimensions:

$$\begin{aligned} a &= 4.41 \pm 0.02\text{\AA} \\ b &= 6.27 \pm 0.02\text{\AA} \\ c &= 13.71 \pm 0.03\text{\AA} \end{aligned}$$

Reflections of the type  $hkl$  were observed only if:

$$h + k + l = 2n,$$

of the type  $hk0$  only if:

$$h = 2n \text{ and } k = 2n,$$

of the type  $h0l$  only if:

$$h + l = 2n,$$

and of the type  $0kl$  only if:

$$k + l = 2n.$$

Hence, the cell is body-centered with an  $00l$  glide plane. The evidence for the existence of the glide plane is the observed extinction of 23 possible re-

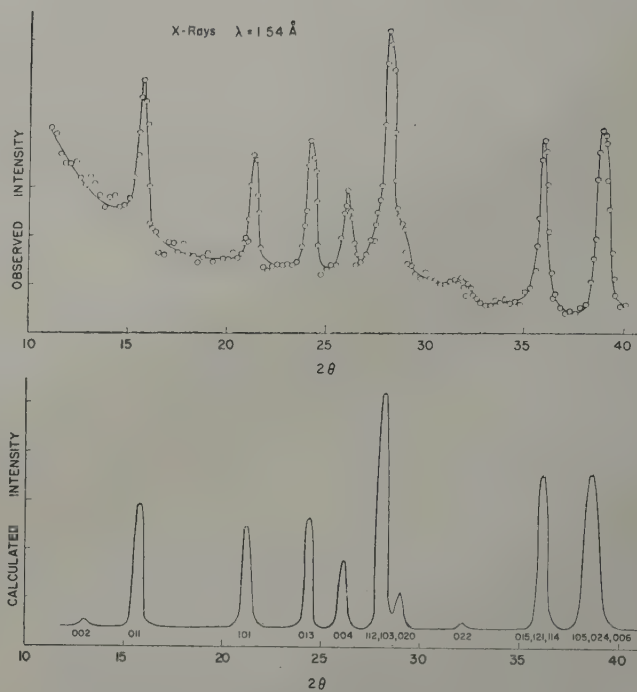


Fig. 1—Comparison of observed and calculated X-ray patterns for  $\text{UAl}_4$ .

flections of the type  $hk0$  with at least one index odd.

There are only two space groups consistent with these data:  $C_{2v}^{22} - I2ma$  and  $D_{2h}^{28} - Imma$ .<sup>3</sup> The possible sets of atomic positions for these space groups are:

$I2ma$ :

$$(0\ 0\ 0; \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}) +$$

$$4: (a) x\ 0\ \frac{1}{2}; x\ \frac{1}{2}\ \frac{1}{2}$$

$$(b) x\ \frac{1}{4}\ z; x\ \frac{3}{4}\ \bar{z}$$

$$8: (c) x\ y\ z; x\ \bar{y}\ \bar{z}; x, \frac{1}{2} + y, \bar{z}; x, \frac{1}{2} - y, z$$

$Imma$ :

$$(0\ 0\ 0; \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}) +$$

$$4: (a) 0\ 0\ 0; 0\ \frac{1}{2}\ 0$$

$$(b) 0\ 0\ \frac{1}{2}; 0\ \frac{1}{2}\ \frac{1}{2}$$

$$(c) \frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}; \frac{3}{4}\ \frac{1}{4}\ \frac{1}{4}$$

$$(d) \frac{1}{4}\ \frac{1}{4}\ \frac{3}{4}; \frac{3}{4}\ \frac{1}{4}\ \frac{3}{4}$$

$$(e) 0\ \frac{1}{4}\ z; 0\ \frac{3}{4}\ \bar{z}$$

$$8: (f) x\ 0\ 0; \bar{x}\ 0\ 0; x\ \frac{1}{2}\ 0; \bar{x}\ \frac{1}{2}\ 0$$

$$(g) \frac{1}{4}\ y\ \frac{1}{4}; \frac{3}{4}\ \bar{y}\ \frac{3}{4}; \frac{3}{4}\ y\ \frac{1}{4}; \frac{1}{4}\ \bar{y}\ \frac{3}{4}$$

$$(h) 0\ y\ z; 0\ \bar{y}\ \bar{z}; 0, \frac{1}{2} + y, \bar{z}; 0, \frac{1}{2} - y, z$$

$$(i) x\ \frac{1}{4}\ z; \bar{x}\ \frac{3}{4}\ \bar{z}; \bar{x}\ \frac{1}{4}\ z; x\ \frac{3}{4}\ \bar{z}$$

$$16: (j) x\ y\ z; x\ \bar{y}\ \bar{z}; x\ \bar{y}\ \bar{z}; x\ y\ z; x, \frac{1}{2} + y, \bar{z}; x, \frac{1}{2} - y, z; x, \frac{1}{2} - y, z; x, \frac{1}{2} + y, \bar{z}$$

Though density measurements on different samples were found to vary somewhat, they were all within the range  $5.7 \pm 0.3$  g per cu cm. If it is assumed that the unit cell contains four formula weights of  $\text{UAl}_4$ , it is 6.5 g per cu cm. If there were as many as eight uranium atoms per unit cell, the

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density would be in excess of 8.5 g per cu cm. Therefore the cell contains four uranium atoms.

If the uranium atoms occupied four-fold positions (a), (b), (c) or (d) of *Imma* or (a) of *I2ma*, for reflections of the type 00*l* the uranums would all be in phase and the reflections should all be fairly uniformly strong. However, the reflections of this type not suppressed by the space group were observed to vary from very strong to very weak. Hence the uranium atoms must occupy either positions (e) of *Imma* or (b) of *I2ma*. By a proper choice of the origin for positions (b) of *I2ma*, so the uranums all lie in planes  $x/a = 0$  and  $x/a = \frac{1}{2}$ , these positions may be made equivalent. It was found that a parameter of  $z/c = 0.111$  fits the observed intensities quite well.

### Determination of the Stoichiometric Formula

Since the space group requires that the number of aluminum atoms per unit cell be a multiple of four, and since there are four uranium atoms per unit cell, the ideal cell must contain four formula weights and the formula must be of the type  $UAl_x$ .

Chemical analyses, as did the density measurements, suggest that the structure occurs over a range of composition. Various samples, which by spectrographic methods were found to contain only traces of impurities and the X-ray patterns of which showed no lines other than those of the compound, were found to have uranium compositions ranging from 64.2 to 66.3 pct by weight. This corresponds to a range in the formula of from  $UAl_{4.0}$  to  $UAl_{4.5}$ . Hence these data yield little information other than that the ideal formula must be either  $UAl_4$  or  $UAl_5$ .

However, it may be shown, on the basis of the atomic radii of uranium and aluminum and the symmetry of the possible space groups, that the formula must be  $UAl_4$ . On the basis of the atomic diameters of the two elements, the U-Al interatomic distance should not be less than 2.73 Å, and the Al-Al distance should be about 2.7 Å.

Positions (a), (c), (d), (f), (g), (i), and (j) of space group *Imma* would all require either a U-Al distance or an Al-Al distance to be less than 2.3 Å. Hence the aluminums must not occupy these positions. It is found, when the remaining three sets of positions are considered, that to satisfy the atomic radii, not more than 16 aluminum atoms may occupy the unit cell; they must be in a set of four in positions (b), a set of four in (e), and a set of eight in (h).

For space group *I2ma*, to satisfy the atomic radii, the 16 aluminums must be in a set of four in (a), a set of four in (b), and a set of eight in general positions (c).

### Determination of the Aluminum Positions

Except for the  $x$  parameters, positions (b), (e), and (h) of *Imma* are equivalent to (a), (b), and (c) of *I2ma*. It was found that to satisfy the interatomic distances, the aluminum atoms must lie in planes  $x/a = 0$  and  $x/a = \frac{1}{2}$ , as described by *Imma*, or very nearly so. It was assumed that this is the case.

A set of approximate aluminum positions for space group *Imma*, chosen to be consistent with the observed X-ray intensities and the atomic radii, are:

- 4 Al in (b)
- 4 Al in (e),  $z/c = -0.111$
- 8 Al in (h),  $y/b = -0.033$ ,  $z/c = 0.314$

A comparison of the observed and calculated X-ray patterns for these positions is shown in Fig. 1. The observed pattern was obtained using a North

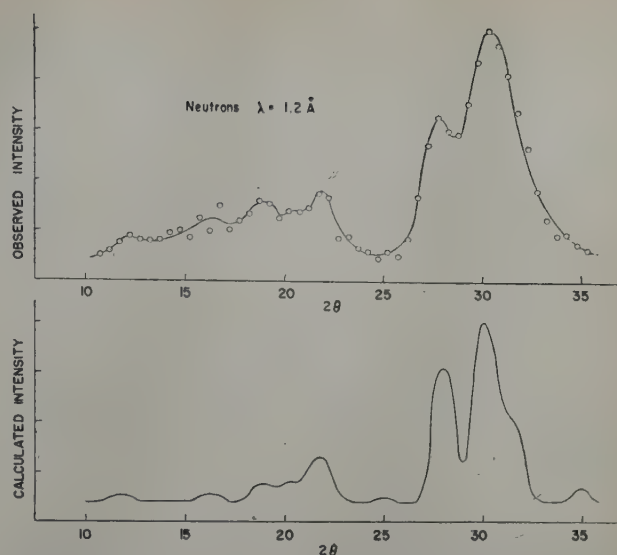


Fig. 2—Comparison of observed and calculated neutron patterns for  $UAl_4$ .

American Phillips spectrometer. The pattern was calculated using the formula:

$$I \propto \frac{(1 + \cos^2\theta) pF^2}{\sin^2\theta \cos \theta}$$

The line widths were chosen to correspond to those observed. An effort to refine these parameters by a Fourier synthesis of the electron density projected on the  $xy$  plane failed. In spite of the fact that the crystal used was quite small, its absorption coefficient was large enough and its shape sufficiently irregular to make accurate determination of the structure factors impossible.

Since the scattering factor of uranium is about seven times that of aluminum, the general characteristics of the calculated diffraction pattern are not very sensitive to variations in the aluminum positions. However, for neutrons the scattering factor of uranium is only slightly more than twice that of aluminum. Hence, the neutron diffraction pattern should provide valuable evidence for the light atom positions. A neutron pattern was obtained and is shown in Fig. 2, compared with the calculated pattern for the aluminum positions listed above. The intensity was taken to be proportional to:

$$\frac{1}{\sin \theta \cos \theta} pF^2$$

Table I. Interatomic Distances of  $UAl_4$

| Atom    | No. of Neighbors | Kind of Neighbors | Distance, Å |
|---------|------------------|-------------------|-------------|
| U (4e)  | 3                | Al (4e)           | 3.14        |
|         | 4                | Al (4b)           | 3.10        |
|         | 4                | Al (8h)           | 3.02        |
|         | 2                | Al (8h)           | 3.30        |
| Al (4e) | 3                | U (4e)            | 3.14        |
|         | 4                | Al (4b)           | 3.10        |
|         | 4                | Al (8h)           | 2.79        |
|         | 2                | Al (8h)           | 3.09        |
| Al (4b) | 4                | U (4e)            | 3.10        |
|         | 4                | Al (4e)           | 3.10        |
|         | 2                | Al (4b)           | 3.14        |
|         | 2                | Al (8h)           | 2.57        |
| Al (8h) | 2                | U (4e)            | 3.02        |
|         | 1                | U (4e)            | 3.30        |
|         | 2                | Al (4e)           | 2.79        |
|         | 1                | Al (4e)           | 3.09        |
|         | 1                | Al (4b)           | 2.57        |
|         | 2                | Al (8h)           | 2.81        |
|         | 1                | Al (8h)           | 3.56        |
|         | 1                | Al (8h)           | 2.72        |

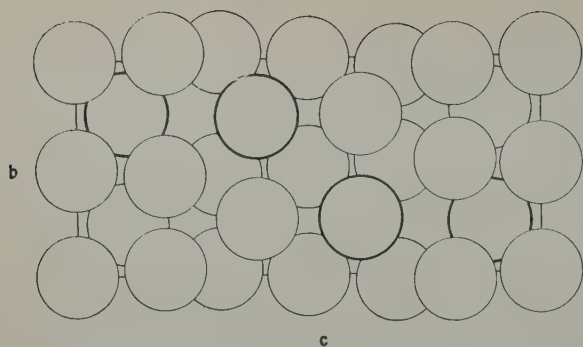


Fig. 3—Unit cell of  $UAl_4$  projected along  $a$  axis. Uranium atoms shown in heavy outline.

The line widths were again chosen to correspond to the observed pattern.

### Summary and Discussion

The Al-rich, U-Al intermetallic compound has the formula  $UAl_4$ . Its unit cell is body-centered orthorhombic,  $a = 4.41\text{\AA}$ ,  $b = 6.27\text{\AA}$ , and  $c = 13.71\text{\AA}$ . The cell contains four formula weights and the space group is either  $I2ma$  or  $Imma$ . The atoms occupy the following positions of  $Imma$ :

|         |                                                                                                                       |
|---------|-----------------------------------------------------------------------------------------------------------------------|
|         | $(0\ 0\ 0; \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}) +$                                                                  |
| 4 U in  | (e) $0\ \frac{1}{4}\ z; 0\ \frac{3}{4}\ \bar{z}; z/c = 0.111$                                                         |
| 4 Al in | (e) $0\ \frac{1}{4}\ z; 0\ \frac{3}{4}\ \bar{z}; z/c = -0.111$                                                        |
| 4 Al in | (b) $0\ 0\ \frac{1}{2}; 0\ \frac{1}{2}\ \frac{1}{2}$                                                                  |
| 8 Al in | (h) $0\ y\ z; 0\ \bar{y}\ \bar{z}; 0, \frac{1}{2} + y, \bar{z}; 0, \frac{1}{2} - y, z$<br>$y/b = -0.033\ z/c = 0.314$ |

The number and kinds of nearest neighbors and the interatomic distances for the various atoms in the unit cell are given in Table I. With the exception of the Al-Al distance of  $2.57\text{\AA}$ , the interatomic distances are consistent with the separations pre-

dicted by the sum of the atomic radii. Though the distances reported are not highly accurate—since the light atom positions are only approximate—it is possible that this separation may be somewhat less than the atomic diameter of aluminum given by Goldschmidt. Axon and Hume-Rothery have found that the apparent atomic radius of aluminum in its face-centered cubic structure is large.<sup>4</sup> They predict that the corrected atomic diameter of aluminum is probably less than  $2.71\text{\AA}$ .

The distribution of the atoms in the unit cell as viewed along the  $a$  axis is shown in Fig. 3. The ones shown in heavy outline are uranium. The atoms are arranged in two layers parallel to the  $yz$  plane at  $x/a = 0$  and  $x/a = \frac{1}{2}$ . The coordination numbers are: for uranium, 13; for the aluminum atoms in (b), 12; in (e), 13; and those in (h), 11.

The chemical analyses and density measurements, which are somewhat inconsistent with the ideal structure, may be explained by assuming either that some uranium sites are unoccupied or that some are occupied by aluminum atoms.

There are numerous structures in which such lattice defects exist.  $CuSn$ , which has the nickel arsenide structure, is invariably found to have a deficiency of tin of about 4.6 atomic pct. A similar situation exists in the phase  $CuAl$ . Lead dioxide is known to retain its structure down to the composition  $PbO_{1.66}$ . Other compounds having defect structures are  $NaWO_3$ ,  $\gamma-Al_2O_3$ , and  $FeS$ , all of which have cation deficiencies.  $NaWO_3$  apparently retains its structure with less than one third of the sodium sites occupied.

An interesting similarity between this structure and the simple cubic structure of  $UAl_3$  exists. This is illustrated in Fig. 4 which compares unit cells of the two structures. The eight-fold aluminum atoms in  $UAl_3$  have been omitted.

It is clear from Fig. 4 that the  $UAl_4$  unit cell, except for the eight-fold aluminum atoms, could be constructed from plates of  $UAl_3$ . The plates would have for their faces 110 planes of the cubic structure and would be of a thickness equal to the spacing of the 110 planes of  $UAl_3$ . The normal to the planes would be parallel to the  $c$  axis of  $UAl_4$ .

Actually the  $UAl_3$  cell would have to be slightly expanded for this construction to be possible. The U-U separation in  $UAl_4$  is about 3.5 pct greater than it is in  $UAl_3$ . However, the cubic symmetry is almost perfectly maintained. For this to be so, the U-U separation in the  $bc$  plane,  $a$ , and  $b/\sqrt{2}$  would have to be equal. These three distances are respectively,  $4.37\text{\AA}$ ,  $4.41\text{\AA}$ , and  $4.43\text{\AA}$ .

Hence the structure may be thought of as  $UAl_3$  plates held together by extra aluminum atoms.

### Acknowledgment

The author is indebted to M. A. Bredig under whose direction and guidance this work was done, C. G. Shull who measured the neutron diffraction pattern, and R. O. Williams who prepared the samples used in this work.

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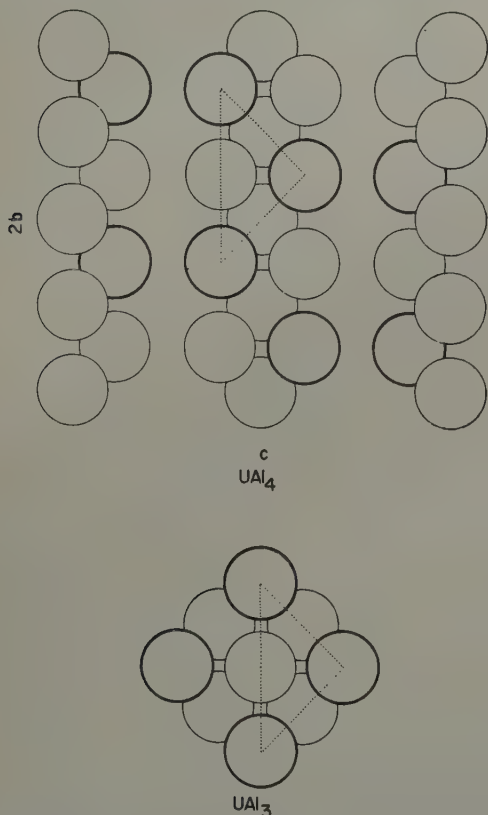


Fig. 4—Comparison of two unit cells of  $UAl_4$ , with the eight-fold Al atoms omitted, and a unit cell of  $UAl_3$ . Analogous units in the two structures are shown with dotted lines. Uranium atoms are shown in heavy outline.



# Solidification of Lead-Tin Alloy Droplets

by J. H. Hollomon and D. Turnbull

THERE is a large body of evidence<sup>1-3</sup> indicating that solidification during the liquid-solid transition is usually induced by heterogeneities present in the liquid. By dispersing liquid metals into small droplets, the impurities responsible for catalyzing solidification are isolated within a small number of these droplets. The effect of the foreign body therefore is restricted to a single drop by this technique. Thus upon cooling below the melting temperature, solidification is initiated by homogeneous nucleation in the majority of the droplets that do not contain impurities.

In the case of solidification of liquid metals, the activation energy for nucleation is so great that its rate changes by orders of magnitude for a change in temperature of only several degrees centigrade.<sup>4</sup> Effectively homogeneous nucleation occurs at a critical temperature upon continuous cooling. Thus by microscopic observation of single particles during cooling, a temperature at which the rate of homogeneous nucleation becomes sensible can be determined.<sup>5</sup> Since at the temperatures at which nucleation occurs in the absence of impurities the rate of crystal growth is extremely rapid, the temperature at which the entire particle solidifies is very nearly the temperature at which the nucleation of the solidification occurs. Thus for liquids that freeze at high temperatures the onset of nucleation can be established by simply observing the temperature at which the marked heat evolution and increase in brightness of the particle occur. For liquids that freeze at lower temperatures the onset of nucleation can be determined by a rumpling and change in shape of the particle resulting from its solidification. The microscopic technique for observing the solidification of small particles has already been described.<sup>5</sup>

In earlier papers the nucleation of solidification of pure metals<sup>6, 7</sup> and of alloy systems<sup>7</sup> showing complete liquid and solid solubility have been described. In the present paper, the observations are extended to a simple eutectic system (Pb-Sn) where the possibility of the formation of two solid phases exists.

Metals for the investigation were obtained from the American Smelting and Refining Co. in the form of pure lead and pure tin, 99.8 and 99.9 pct purity, respectively. An ingot of each of the pure metals was made into shot by heating the metals at a temperature about 50°C in excess of the melting point and pouring the liquid slowly into a container of water at 15°C. Samples of the shotted pure metals were weighed out to make alloys containing 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, and 90 atomic pct Pb. Samples of each alloy were then melted in separate beakers. Each melt was poured through a pyrex

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Table I. Analyses of Poured Metal

| Nominal Tin, Pct | Actual Tin, Pct |
|------------------|-----------------|
| 90               | 91.4            |
| 60               | 60.6            |
| 40               | 41.7            |
| 30               | 31.0            |
| 20               | 23.0            |
| 10               | 10.2            |

funnel into a cylindrical mold ( $\frac{5}{8}$  in. ID). The casting solidified in 10 to 20 sec. The inside of the mold as well as the funnel through which the metal was poured were coated with graphite to eliminate adherence of the metal. Analyses were performed on some of the compositions and are given in Table I.

The compositions also were checked for these samples and for those that were not analyzed by determining the spread between the liquidus and the solidus upon melting the small metal particles. These measurements agreed as well with the nominal compositions as the analyses listed above.

## Results

The results of the supercooling experiments for the several alloys are summarized in Table II and plotted on the constitution diagram in Fig. 1. Data for the pure lead and pure tin were taken from earlier investigations.

The values for the maximum supercooling of the several alloys are the average of several determinations on a number of drops of each alloy. The maximum value in any determination was within about 2 pct of the average. For the alloys containing from 20 to 60 atomic pct Sn, inclusive, two marked changes of the surface structure were observed upon cooling. At the higher temperature, after the first appearance of the solid phase it continued to grow slowly at a constant temperature and then stopped. At the lower temperature the alteration of surface structure was abrupt. For the alloys containing from 70 to 95 atomic pct Sn, inclusive, an abrupt change in surface structure was observed at a single critical temperature.

Table II. Results of Supercooling Experiments

| Tin, Atomic Pct | Temperature, °C |                    |                           |
|-----------------|-----------------|--------------------|---------------------------|
|                 | Liquidus        | 1st Solidification | 2nd Abrupt Solidification |
| 0               | 327             | 247 <sup>5</sup>   | none                      |
| 10              | 310             | 275                | none                      |
| 20              | 298             | 256                | 170                       |
| 30              | 281             | 238                | 159                       |
| 40              | 261             | 230                | 158                       |
| 50              | 241             | 205                | 158                       |
| 60              | 218             | 170                | 158                       |
| 70              | 192             | 148                | none                      |
| 75              | 185             | 135                | none                      |
| 80              | 193             | 120                | none                      |
| 85              | 201             | 142                | none                      |
| 90              | 210             | 150                | none                      |
| 95              | 221             | 145                | none                      |
| 100             | 232             | 127 <sup>8</sup>   | none                      |



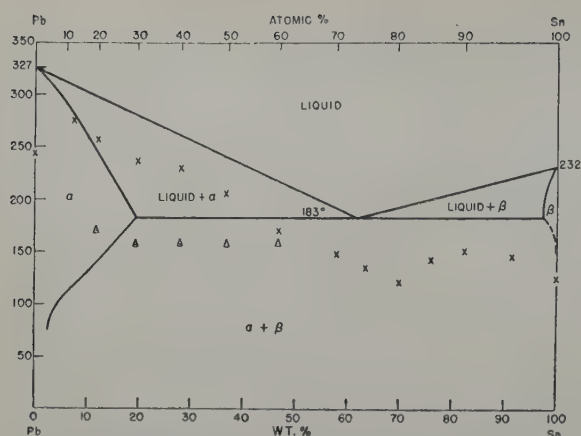


Fig. 1—Equilibrium diagram of Pb-Sn system with solidification temperature of small alloy droplets indicated.

The alloy containing 20 atomic pct Sn completed its solidification at a temperature of about 170°C. However, in all these experiments summarized in Table II and Fig. 1 the cooling time from the maximum temperature (where the drop was liquid) to the temperature of complete solidification was of the order of 10 min. It was believed that the second critical temperature for complete solidification of the 20 and 30 atomic pct alloys resulted from segregation due to lack of equilibration of the composition. Thus a second set of experiments were performed with the 20 pct alloy in which the specimen was held at a temperature of about 220°C for several hours. This treatment resulted in less segregation as determined metallographically than did the more rapid cooling, and the lower critical temperature was not observed. However, it is believed that the two critical temperatures for the 40, 50, and 60 pct alloys would be observed if the equilibration with respect to composition was complete.

A droplet from each of the several compositions was cross-sectioned and examined metallographically after solidification. Typical micrographs are presented in Figs. 2, 3, 4, and 5. Fig. 2 is the micro-

structure of the alloy containing 70 pct Pb. The alloy of Fig. 3 contains 25 pct Pb and that of Figs. 4 and 5, 15 pct Pb. All the micrographs are at 500 magnification excepting that Fig. 5 was taken at 100X. In Fig. 2 the light constituent is the tin phase trapped by the dendritic arms of the lead. Conversely, in Figs. 4 and 5, small particles of lead have been trapped by the dendritic arms of tin.

### Discussion

In the phase diagram in Fig. 6, the liquidus lines have been extrapolated into the metastable region. In an alloy of 50 atomic pct Sn, lead nucleates homogeneously at the temperature marked *x*; the alloy being significantly supercooled (approximately 40°C). As the small droplet is further cooled the composition of the liquid tends to follow the  $\alpha$ -liquidus line and its extension into the region of metastability. At the temperature marked with the triangle that liquid becomes sufficiently supercooled with respect to the  $\beta$ -liquidus that tin nucleates. Thereafter both lead and tin crystals grow. The actual composition of the liquid phase when tin nucleates must fall on the extended  $\alpha$ -liquidus and is marked with a circle at the same temperature as that of the triangle. For the alloy containing 10 atomic pct Sn the droplet solidified completely as soon as nucleation of lead took place.

For the 20 and 30 atomic pct Sn alloys the solidification began with the formation of a lead-rich phase at the temperatures marked *x* and was completed gradually if the temperature was lowered slowly. Consider now an alloy containing 70 atomic pct Sn. Upon supercooling approximately 45°C, the alloy completely solidifies. After the formation of the lead-rich nucleus the composition of the residual liquid is given by the  $\alpha$ -liquidus composition at that temperature. At this composition and temperature the solution is already supercooled below the temperature of rapid nucleation of the tin-rich phase in the presence of lead indicated by the circle. Thus a line joining the points marked with *x* in Fig. 6 represents the temperature at which the lead-rich phase

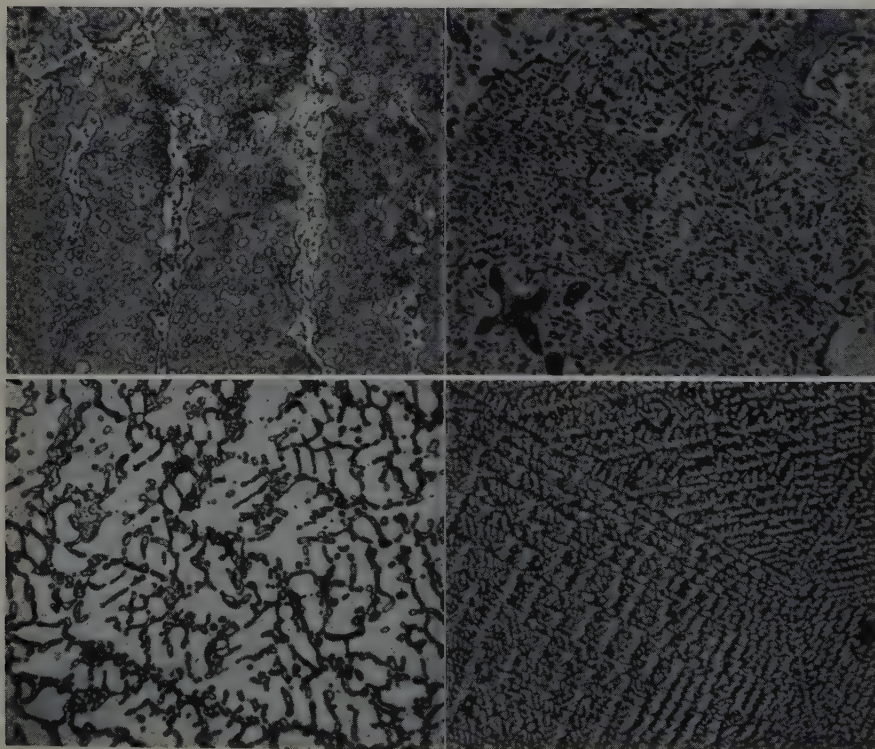


Fig. 2 (upper left)—Microstructure of alloy droplet after solidification, 30 atomic pct Sn. X500.

Fig. 3 (upper right)—Microstructure of alloy droplet after solidification, 75 atomic pct Sn. X500.

Fig. 4 (lower left)—Microstructure of alloy droplet after solidification, 85 atomic pct Sn. X500.

Fig. 5 (lower right)—Microstructure of alloy droplet after solidification, 85 atomic pct Sn. X100.



first nucleates from the liquid solution. The triangles represent the temperature at which the tin-rich phase subsequently nucleates from the supercooled liquid solution. Since the nucleation of the tin-rich phase occurs at a temperature and composition on the extended liquidus line the temperature at which the tin-rich phase first forms is independent of the compositions of the alloy for percentages less than the 70 atomic pct Sn.

Consider now an alloy containing 90 atomic pct Sn. It is noted that complete solidification is accomplished by cooling this alloy to a single temperature even though it is not supercooled below the extended  $\alpha$ -liquidus line. The interpretation of this result is that tin nucleates first with a supercooling of approximately 75°C following which the composition of the liquid becomes that given by the extended  $\beta$ -liquidus line. At this composition the temperature is below that necessary to nucleate the lead-rich phase. Thus immediately upon the formation of the first tin-rich nucleus and following its growth, the liquid is supersaturated and supercooled sufficiently for the lead-rich phase to nucleate and grow. Particles of the lead-rich phase will nucleate within the liquid trapped in the interstices of the tin-rich phase as illustrated in Figs. 4 and 5. Thus the curve joining the squares gives the temperature at which the tin-rich phase first nucleates. With an alloy containing approximately 80 atomic pct Sn the temperatures at which the tin and lead-rich phase nucleate are very nearly the same.

The fact that the tin-rich phase that forms following the formation of the lead-rich phase solidifies at a temperature of about 10° above the curve of temperature of first solidification of tin-rich alloys indicates that possibly the lead-rich phase has a mild catalytic effect on the nucleation of the tin-rich phase. The effect is less than 10° and amounts to only a little more than the experimental errors. Also there is some additional error due to the extrapolation of the  $\alpha$ -liquidus curve.

In some systems in which two solid phases may form from a single liquid solution one of the phases may catalyze the nucleation of the second phase. Experiments in other systems should be performed to determine the prevalence of such catalytic action.

The degree of supercooling is determined by the differences in free energy between the solid and the liquid and upon the interfacial free energy between that solid and the melt. An interpretation of the slight decrease in the amount of supercooling with a small addition of tin to lead or of lead to tin may be that this addition decreases the interfacial tension between the solid that nucleates and the liquid from which it forms.

In pure metals it is possible to calculate from the theory of homogeneous nucleation and from the maximum supercooling of small droplets the interfacial free energy between the liquid and solid phases. However, in an alloy system, for a liquid of a given composition both the interfacial free energy between this liquid and solid and the free energy difference between this liquid and the solid will be a function of the composition of the solid. Thus even though the free energy as a function of composition is known it is not possible to calculate the interfacial free energy unless the composition of the nucleus is known or the dependence of the interfacial free energy on the composition is known. The functional relationship between the interfacial free energy between liquid and solid and the composition of the

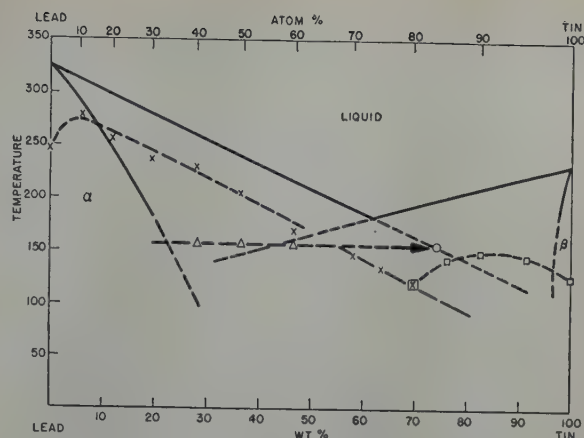


Fig. 6—Solidification temperatures of Pb-Sn alloy droplets in relation to extended equilibrium lines.

solid can in principle be determined experimentally. Theoretical analysis of these experimental results in terms of nucleation theory will not be possible until these measurements have been made.

### Summary

1—The solidification of Pb-Sn alloy droplets (30 to 50 micron diam) was observed as a function of composition by a microscopic technique.

2—On the lead-rich side of the eutectic the initial solidification temperature,  $T_i$ , is about 35° to 45°C below the liquidus,  $T_l$ , excepting that for pure lead  $T_m - T_i = 80^\circ$ .

3—On the tin-rich side of the eutectic  $T_m - T_i \sim 60^\circ$  to 75°C excepting that for pure tin  $T_m - T_i = 110^\circ$ .

4—In the lead-rich alloy a second temperature of abrupt solidification  $T_i \sim 160^\circ$  and independent of composition was observed. It is believed that  $T_i$  is the initial solidification temperature of the tin-rich solution that remains liquid after the formation and growth of the lead-rich crystalline phase.

5—There is some evidence that the lead-rich crystalline phase has a mild catalytic effect on the formation of nuclei for the growth of the tin-rich solid solution.

### Acknowledgment

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# Creep Characteristics of Some Platinum Metals at 1382°F

by R. H. Atkinson and D. E. Furman

HITHERTO the practical creep testing of precious metals has received little or no attention. The only previous creep tests of precious metals have been made with wires under conditions such as to yield much more rapid rates of creep than in engineering tests.<sup>1, 2</sup> Up to the present time the value of creep bars of adequate size, in the absence of real need for engineering data, has deterred investigators. However, the increasing use of platinum at high temperatures has demonstrated the need for reliable creep data for the guidance of engineers, especially those engaged in designing certain specialized chemical plant equipment. In order to supply this need, creep tests were conducted at 1382°F (750°C) on 0.290 in. diam specimens of platinum, 90 pct Pt, 10 pct Rh and palladium.

The platinum was high purity, nominally 99.95 pct Pt. The 90 pct Pt, 10 pct Rh was of the same high quality as is used for making gauzes for the catalytic oxidation of ammonia. The palladium was also of high purity; two batches of palladium bars were tested, one deoxidized with calcium boride and the other with aluminum. Spectrographic examination of the palladium confirmed its good quality; the only significant impurities apart from the residual deoxidizers were traces of silicon and lead.

## Procedure

The creep bars, which were furnished by Baker and Co. to our specification, were 6¾ in. in overall length with a 4½ in. (4 in. gage length) reduced section 0.290 in. in diam and had the ends threaded (¾-NC16). It may be of interest that the bars were valued at up to \$600 each. The specimens were supplied in a 50 pct cold-worked condition to facilitate attachment of the creep extensometer, which was of the push rod type. Because of the softness of the platinum and palladium, the extensometer rings were secured to the test section by means of circular knife edges instead of the usual pointed set screws. The extensometer rods extended through the bottom of the furnace and readings were taken with a 0.0001 in. "Last Word" dial gage fastened to the rods for the duration of the test. The bars were directly loaded by hanging weights from the lower specimen grip. All tests were conducted at 1382°F ± 2°F, and an effort was made to maintain the temperature gradient over the test section within 2°F. The ends of the furnace tube were packed with asbestos wool, which allowed a very slow circulation of air through the tube.

Annealing was accomplished in the creep furnace before the load was applied. The platinum and palladium specimens were annealed at the test tem-

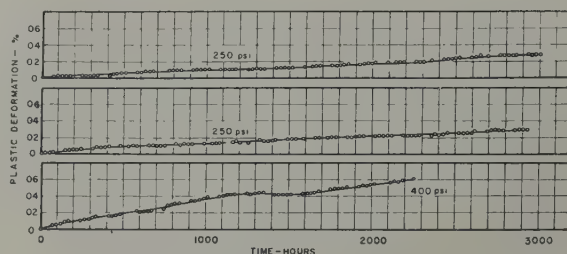


Fig. 1—Platinum creep curves at 1382°F (750°C).

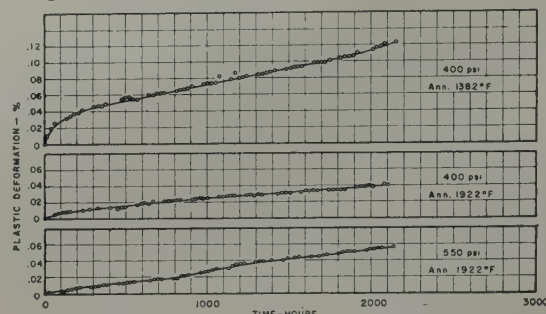


Fig. 2—Platinum, 10 pct Rhodium creep curves at 1382°F.

perature for about 17 and 24 hr respectively; in the case of the rhodiplatinum it was found expedient to anneal for 1 hr at 1922°F (1050°C). Pilot samples cut from the same stock as the bars were used to check annealing procedures. Pertinent measurements of grain size and hardness were recorded.

## Results and Discussion

The creep data obtained are given in Table I and the creep curves are plotted in Figs. 1, 2, and 3.

Two platinum specimens, tested under a stress of 250 psi, had almost identical creep rates at 2000 hr, namely 0.000008 and 0.000009 pct per hr. A third platinum specimen, stressed at 400 psi, had a creep rate at 2000 hr of 0.000026 pct per hr; the reason for a rather sharp decrease in creep rate during the period from 1200 to 1600 hr is unknown.

As it was thought that 90 pct Pt, 10 pct Rh would have a lower creep rate than platinum, the first sample was tested at 400 psi; however, the creep rate was approximately 50 pct greater. Microexamination revealed that differences in grain size might be responsible for the unexpected result, as annealing at 1382°F developed an average grain diameter of 0.0021 in. in the rhodiplatinum specimen compared with 0.004 in. in the platinum bar. Annealing the alloy for 1 hr at 1922°F (1050°C) increased the average grain diameter to 0.0032 in. and materially improved the creep resistance, making it much better than platinum. A second specimen annealed at 1922°F (1050°C) and tested under a stress of 550 psi had a creep rate of 0.000022 pct per hr at 2000 hr, which was still substantially lower than that shown by the specimen annealed at 1382°F (750°C) and stressed at only 400 psi.

In contrast to the creep behavior of the platinum and rhodiplatinum specimens, the palladium bars, whether deoxidized with calcium boride or aluminum, were characterized by high first stages of creep. However, after about 1200 hr of test, the creep

<sup>1</sup> S. Dushman, L. W. Dunbar, and H. Huthstainer: Creep of Metals. *Journal of Applied Physics* (1944) 15, pp. 108-124. Paper includes measurements of rate of creep of Pt wires (0.010 in. diam).

<sup>2</sup> R. P. Carreker, Jr.: Plastic Flow of Platinum Wires. *Journal of Applied Physics* (1950) 21, pp. 1289-1296.

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rates decreased rather rapidly to much smaller values. As the changes in creep rate occurred after approximately 1200 hr regardless of whether the specimens were stressed at 250 or 150 psi, it was decided to pretreat another specimen at the test temperature for a similar length of time. This pretreatment of the unstressed creep specimen completely eliminated the high first stage of creep and may have improved the secondary creep rate too. Incidentally the specimen did not change in length during pretreatment. It was thought at first that the good effect of the extended anneal might be associated with further stress relief or an increase in grain size, but measurements of hardness and grain size did not support this view. However, something else had been happening which might affect

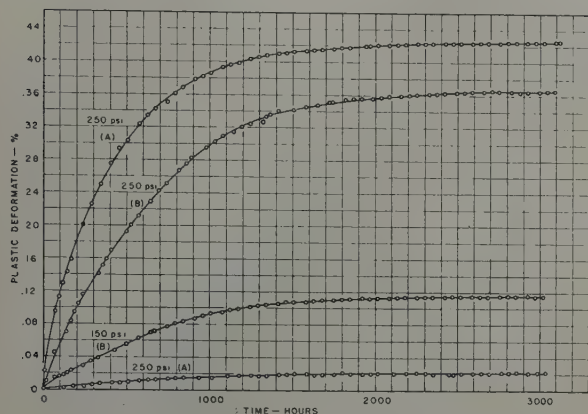


Fig. 3—Palladium creep curves at 1382°F.  
A—Bar deoxidized with aluminum.  
B—Bar deoxidized with calcium boride.

the creep rate. Microexamination of bars after tests of 3000 hr duration revealed intergranular attack and formation of subscale to a depth of about 0.055 in., Fig. 4, and the rate of penetration indicated that the major part of this internal oxidation probably occurred during the first thousand hours at testing temperature. The improvement effected by the extended anneal might be due to its affording an opportunity for the subsurface reaction to reach equilibrium before the load was applied.

A comparison of the creep strengths of the three materials at 1382°F (750°C) on the basis of the estimated stresses required to give a creep rate of 0.00001 pct per hr at 2000 hr (or 3000 hr in the case of palladium) may be made from the log stress-log creep rate plot of Fig. 5. For platinum and 90 pct Pt, 10 pct Rh stresses of 270 psi and 340 psi, respectively, would give creep rates of 0.00001 pct per hr at 2000 hr. In the case of palladium it is esti-

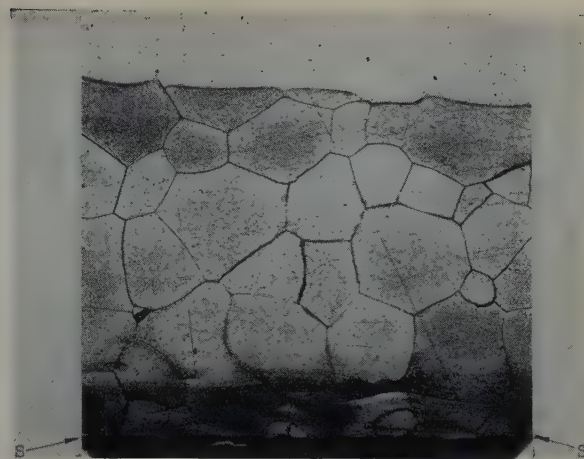


Fig. 4—Palladium creep bar after 3090 hr test. Longitudinal section shows intergranular attack and formation of subscale extending to a considerable distance below the surface (SS). True depth of attack as observed in a cross-section was 0.052 in. Etch: Electro, AC; 5 pct NaCN. X28.

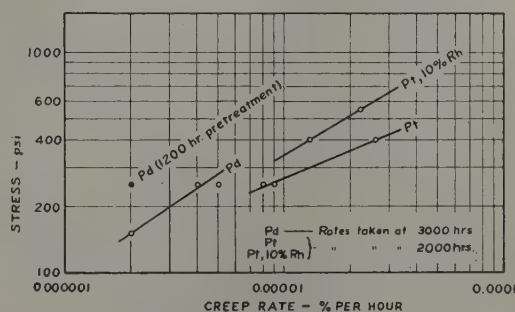


Fig. 5—Creep data at 1382°F.

mated that a stress of 440 psi would give the same creep rate at 3000 hr. The evaluation of the creep strength of palladium is made at 3000 hr because the creep data at 2000 hr are influenced by the high first stage, which it was shown later could be eliminated by suitable pretreatment.

The surprising finding that palladium is apparently more creep resistant than either platinum or 90 pct Pt, 10 pct Rh at the given temperature calls for comment. The larger grain size of the palladium does not seem to account adequately for its superiority. It would almost seem as if internal oxidation had strengthened the palladium instead of weakening it. The question also arises as to whether very pure palladium free from excess deoxidizer would also be more creep resistant than pure platinum. To answer this question it would be necessary to measure the creep rate of specimens prepared from

Table I. Creep Data for Platinum, Platinum 10 Pct Rhodium and Palladium at 1382°F (750°C)

| Material                       | Annealing Temperature, °F | Average Grain Diam, In. | Stress, Psi | Creep Rate—Pct per Hr X 10 <sup>4</sup> |         |         | Length of Test, Hr | Estimated Stress for Creep Rate of 0.00001 Pct per Hr | Hardness, VHN |            |
|--------------------------------|---------------------------|-------------------------|-------------|-----------------------------------------|---------|---------|--------------------|-------------------------------------------------------|---------------|------------|
|                                |                           |                         |             | 1000 Hr                                 | 2000 Hr | 3000 Hr |                    |                                                       | Before Test   | After Test |
| Platinum                       | 1382                      | 0.0040                  | 250         | 0.08                                    | 0.08    | 0.04    | 3817               |                                                       |               |            |
| Platinum                       | 1382                      | 0.0040                  | 250         | 0.09                                    | 0.09    |         | 2929               |                                                       |               |            |
| Platinum                       | 1382                      | 0.0040                  | 400         | 0.33                                    | 0.26    |         | 2256               | 270                                                   |               | 41*        |
| Platinum                       | 1382                      | 0.0021                  | 400         | 0.40                                    | 0.40    |         | 2153               |                                                       |               |            |
| Platinum                       | 1922                      | 0.0032                  | 400         | 0.17                                    | 0.13    |         | 2107               |                                                       |               |            |
| Rhodium                        | 1922                      | 0.0032                  | 550         | 0.38                                    | 0.22    |         | 2135               | 340                                                   | 74*           | 76*        |
| Palladium (CaB <sub>6</sub> )† | 1382                      | 0.015                   | 250         | 1.43                                    | 0.19    | 0.04    | 3090               |                                                       |               |            |
| Palladium (CaB <sub>6</sub> )† | 1382                      | 0.015                   | 150         | 0.56                                    | 0.08    | 0.02    | 3017               |                                                       | 43            | 42         |
| Palladium (Al)†                | 1382                      | 0.015                   | 250         | 0.87                                    | 0.18    | 0.05    | 3118               | 440                                                   |               |            |
| Palladium (Al)†                | 1382‡                     | 0.015                   | 250         | 0.09                                    | 0.03    | 0.02    | 3032               |                                                       | 41*           | 42         |

\* Pyramidal diamond, 1 kilo load. Other VHN taken with 5 kilo load. † Deoxidizer. ‡ Specimen annealed for 1200 hr before loading.

vacuum cast palladium without the use of deoxidizer.

### Summary

The creep rates of pure platinum, 90 pct Pt, 10 pct Rh and pure palladium at 1382°F (750°C) have been determined using bars 0.290 in. in diam and stresses of 150 to 550 psi in tests lasting up to 3000 hr. The creep rate curves of platinum were normal for stresses of 250 and 400 psi. The creep rate of 90 pct Pt, 10 pct Rh, provided it was given a brief high temperature anneal (1 hr at 1922°F) for grain enlargement, was below that of pure platinum. The creep rate of normally annealed palladium under stresses of 150 and 250 psi was very high for the

first 1200 hr but fell to a low value thereafter. Heating the palladium at 1382°F (750°C) for 1200 hr virtually eliminated the first stage of creep and also lowered the rate in the second stage.

### Acknowledgment

The authors wish to take this opportunity of thanking Baker & Co., of Newark, N. J., for their cooperation both in lending the platinum metals and in preparing the specimens. The authors are grateful to N. B. Pilling, Director of Research, International Nickel Co., for permission to publish these data, to E. M. Wise for suggestions and to W. T. Coughlin and J. W. Whitney for their assistance.

## Technical Note Deformation Texture of Body-Centered Cubic Metal Wires

by W. R. Hibbard, Jr., A. E. Roswell, and A. E. Schuetz

THE drawn wire texture of body-centered cubic iron,<sup>1</sup> tungsten,<sup>2</sup> and molybdenum<sup>3</sup> has been determined to be a [110] direction parallel to the wire axis. The purpose of this study is to extend the available information on body-centered cubic wire textures to other metals and alloys.

Wires were produced using hand wire rolls and dies as given in Table I. In addition, attempts were unsuccessful to draw wires from chromium, vanadium (Vanadium Corp. of America), and tungsten (Cleveland Tungsten Inc.). Although it is known that wires can be made from these materials, suitable techniques were not readily adaptable.

Where necessary, wires were polished and etched to form flat ribbons 0.005 to 0.007 in. thick, and transmission X-ray patterns were taken using molybdenum radiation with the specimen tilted 0 degrees from the perpendicular toward the beam to critically cover the wire axis. Analyses were made of (110), (002), and (112) reflection circles.

Table I. Wires Used in Study

| Metal                        | Source                     | Reduct.<br>in<br>Diam,<br>Pct | Remarks                                               |
|------------------------------|----------------------------|-------------------------------|-------------------------------------------------------|
| $\beta$ brass<br>(51.92 pct) | American Brass Co.         | 78.1                          | Hot worked at 600°C                                   |
| $\beta$ brass<br>(62.5 pct)  | Scovill Mfg. Co.           | 71.2                          | Quenched from 875°C,<br>Cold formed                   |
| Iron                         | Armco                      | 97                            | Cold formed                                           |
| Molybdenum                   | North American<br>Phillips | 93                            | Hot formed starting at<br>550°C, finished at<br>110°C |
| Niobium                      | Rem-Cru                    | 95                            | Cold formed                                           |
| Tantalum                     | Fansteel                   | 97                            | Cold formed                                           |

In all cases reflection maxima indicated the texture to be a single [110] deformation fiber, as illustrated by Fig. 1 for molybdenum. In the case of the hot-worked  $\beta$  brass, a second texture, [100], was also found, but this is believed to be the result of recrystallization since it has been reported for recrystallized molybdenum wires<sup>4</sup> and it was not present in the cold-drawn  $\beta$  brass. The difference

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Fig. 1—Molybdenum wire drawn 93 pct reduction in diam.

Wire axis verticle tilted 10° from perpendicular toward the beam. (110) ring shows maxima at 0°, 60°, and 90° from wire axis, (002) ring at 45° and 90°, and (112) ring at 30°, 55°, 73° and 90° indicating a single [110] texture.

in drawability between the 51.92 pct Cu  $\beta$  brass and the 62.5 pct Cu  $\beta$  brass (containing some grain boundary  $\alpha$  due to incomplete quenching) is quite striking, since the latter could be cold worked readily while the former had to be hot worked to avoid cracking.

### Summary

The deformation texture of drawn body-centered cubic wires of  $\beta$  brass, iron, molybdenum, niobium, and tantalum is essentially a single [110] fiber as predicted by theory.<sup>5</sup>

### Acknowledgment

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# Rapid Tempering of High Speed Steel

by A. E. Powers and J. F. Libsch

THE simultaneous influence of time and temperature upon the tempering process in steel is well known. Hollomon and Jaffe<sup>1</sup> have expressed the effect of time and temperature upon the progress of tempering by a single parameter,  $T (c + \log t)$ ; where  $T$  is the absolute temperature;  $t$ , the tempering time; and  $c$ , a constant characteristic of the steel and treatment. It was found that when hardness data for plain carbon and low alloy steels were plotted vs. this parameter, a master tempering curve was obtained which satisfied all the data for a given steel and a given hardening treatment. Roberts, Grobe, and Moersch<sup>2</sup> successfully applied the tempering parameter to various tool steels, including high speed steel for tempering times ranging from 6 min to 100 hr. The influence of tempering time and temperature upon the physical properties of high speed steel has also been extensively investigated.<sup>2-5</sup>

Recently, the use of induction heating for very rapid tempering treatments has received attention. The authors<sup>6</sup> have shown that tempering treatments of only a few seconds duration may be successfully applied to plain carbon and low alloy steel. However, the influence of such short tempering treatments in high speed steel has not been explored.

Since high speed steel is a highly alloyed steel exhibiting physical reactions during tempering that are often relatively slow and large in magnitude, it is an interesting steel for the study of tempering reactions. It was the purpose of the present investigation, therefore, to study the early progress of reactions leading to secondary hardness in high speed steel, type 6-5-4-2, and to determine if induction-tempering treatments of a few seconds duration are able to produce results equal to those of more conventional long-time tempering cycles.

## Experimental Details

The chemical compositions for two different heats of W-Mo high speed steel used in this study are given in Table I.

Table II summarizes the heat treatment given various groups of specimens cut  $2\frac{1}{2}$  in. long and centerless ground to  $\frac{1}{4}$  in. diam. Hardening treatments consisted of preheating to 1600°F (870°C) for  $\frac{1}{2}$  hr and then oil quenching from 2250°F (1230°C). Heat I was subjected to the high temperature in a salt bath for 3 min, while specimens of heat II were austenitized in a carbon-block muffle furnace for 10 min. Specimens of series E were

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Table I. Chemical Analysis of High Speed Steel

| No. | C    | Mn   | P     | S     | Si   | Cr   | V    | Mo   | W    |
|-----|------|------|-------|-------|------|------|------|------|------|
| I   | 0.79 | 0.25 | 0.016 | 0.011 | 0.35 | 4.02 | 1.94 | 5.20 | 6.15 |
| II  | 0.81 | 0.29 | 0.020 | 0.008 | 0.26 | 3.90 | 1.92 | 4.80 | 6.01 |

Table II. Summary of Hardening and Tempering Treatments

| Series | Heat | Hardening Treatment* | Pre-tempering Treatment | Tempering Treatment                               |
|--------|------|----------------------|-------------------------|---------------------------------------------------|
| A      | I    | Salt bath            | None                    | Induction, 450°F per sec                          |
| B      | I    | Salt bath            | None                    | Induction, 450°F per sec<br>60 sec at temperature |
| C      | I    | Salt bath            | None                    | Salt bath, 1 hr<br>at temperature                 |
| D      | I    | Salt bath            | None                    | Double induction<br>450°F per sec                 |
| E      | II   | Muffle furnace       | -318°F, 1 hr            | Induction, 1300°F per sec                         |
| F      | I    | Salt bath            | -100°F, 2 hr            | Induction, 450°F per sec                          |
| G      | I    | Salt bath            | -100°F, 2 hr            | Salt bath, 1 hr<br>at temperature                 |
| H      | II   | Muffle furnace       | None                    | Lead bath, 10 sec<br>total time                   |
| I      | II   | Muffle furnace       | None                    | Salt bath, 1 hr<br>at temperature                 |

\* Oil quenched from 2250°F.

immediately refrigerated to -318°F (-195°C) in liquid nitrogen following the hardening treatment to transform the major portion of the retained austenite. Specimens of series F and G were subzero cooled to -100°F (-75°C) in a dry ice-alcohol mixture.

Induction tempering was performed with a Lepel high frequency converter operating at a frequency of approximately 300,000 cycles per sec. Heating cycles were controlled and recorded for each specimen using a chromel-alumel thermocouple, percussion welded to the surface of the specimen, and a modified high speed instrument with a timer previously used and described.<sup>7</sup> Temperature oscillation of the specimens, while being held at the tempering temperature, was  $\pm 15^\circ\text{F}$  ( $8^\circ\text{C}$ ).

**Tempering Treatments:** After hardening, specimens were tempered between 900° and 1500°F (480° and 815°C) to study the progress of retained austenite decomposition and secondary hardening. The specimens tempered in salt for 1 hr (series C, G, and I) were considered to represent conventional treatment and are used for comparison with rapid tempering treatments. Several induction-tempering cycles were employed: 1—flash tempering, i.e., induction heating to the tempering temperature and immediately cooling (series A, E, and F); 2—induction heating for 60 sec at temperature (series B); and 3—double-induction tempering by two successive heating and cooling cycles (series D). All specimens tempered by induction were heated at an initial rate of 450°F (250°C) per sec except those of series E, which were heated at an initial rate of 1300°F

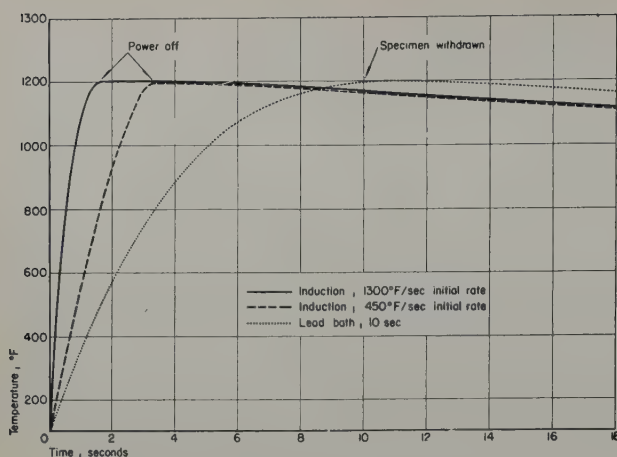


Fig. 1—Representative temperature-time curves for induction-heated and lead bath-heated specimens.

(720°C) per sec. Finally, one series of specimens (series H) was tempered by heating in a lead bath for a total time of 10 sec to determine the possible influence of high frequency induced energy upon the rate of tempering by comparison of lead and induction-tempered samples. All specimens were air-cooled from the tempering temperature.

Fig. 1 shows typical heating and cooling curves for specimens tempered in lead, and by induction, using initial heating rates of 1300°F (720°C) and 450°F (250°C) per sec. Specimens induction tempered for 60 sec were heated at an initial rate of 450°F (250°C) per sec and held at temperature by power impulses from the converter.

With very rapid tempering treatments involving little or no time at the tempering temperature, the degree of tempering which may take place during heating and cooling may assume significant proportions. Accordingly, effective times at temperature were calculated from the recorded heating and cooling curves for the specimens tempered by induction and in lead using the step-by-step integration method proposed by Hollomon and Jaffe.<sup>1</sup> This

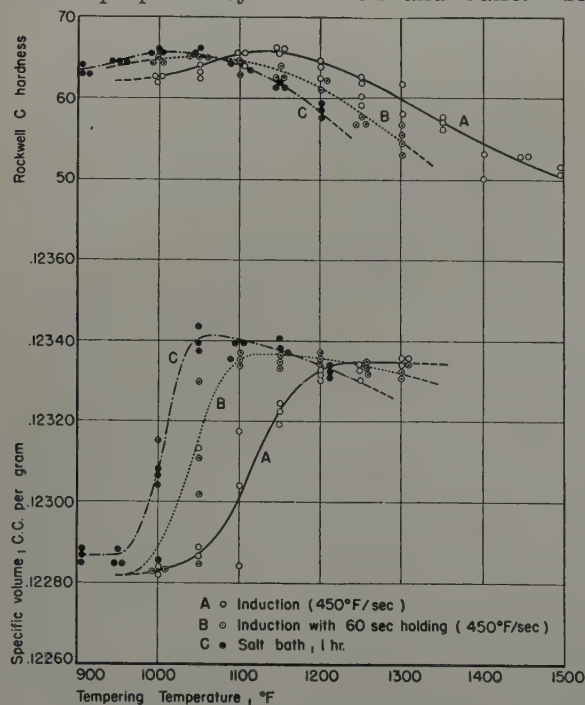


Fig. 2—Hardness and specific volume vs. temperature for various tempering cycles, series A, B, and C.

method utilizes the incremental equation:

$$P = T \log \left( \frac{\Delta t}{t_0} + 10^{P_s/T} \right) \quad [1]$$

where  $P$  is the value of the tempering parameter;  $T$ , the absolute temperature, °Rankine;  $\Delta t$ , an increment of time;  $t_0$ , the constant ( $10^{-12.5}$  for the steel used in this investigation); and  $P_s$ , the value of  $P$  at the beginning of the interval  $\Delta t$ .

The value of  $P$  for any tempering cycle may be found from this equation by integrating step-by-step over suitable intervals of time from the beginning of the cycle to the end. From the value of  $P$  thus obtained, and the basic relation  $P = T (c + \log t)$ , the effective time  $t$  at a given temperature  $T$  can be calculated. In the induction-heating cycles used in this study, it was found that the tempering which occurred at more than 40°F (22°C) below the tempering temperature could be neglected in the calculation of the total value of  $P$ . The effective tempering times at temperature as thus determined varied from 4.2 sec at 1500°F (815°C) to 9.0 sec at 900°F (480°C) for the specimens tempered by induction heating; and from 7.0 sec at 1500°F (815°C) to 12.0 sec at 900°F (480°C) for the specimens heated in lead. The proper effective tempering times were utilized in plotting the data obtained.

**Physical Testing:** After tempering, all specimens were centerless ground to remove approximately 0.004 in. from the surface, polished to remove grinding marks and then tested to determine specific volume and Rockwell C hardness. Specimens of series A, B, C, D, F, and G were subsequently fractured in the bend test.

Specific volume measurements were made by the weight-in-air, weight-in-water method, and all precautions were observed to insure maximum accuracy. Weighing was conducted to the nearest 0.2 mg and the temperature was measured to the nearest 0.1°C.

Bend tests were performed on 1/4 in. diam specimens in an enclosed bend-test fixture having supports 2 in. apart and a loading plunger with a 3/8 in.

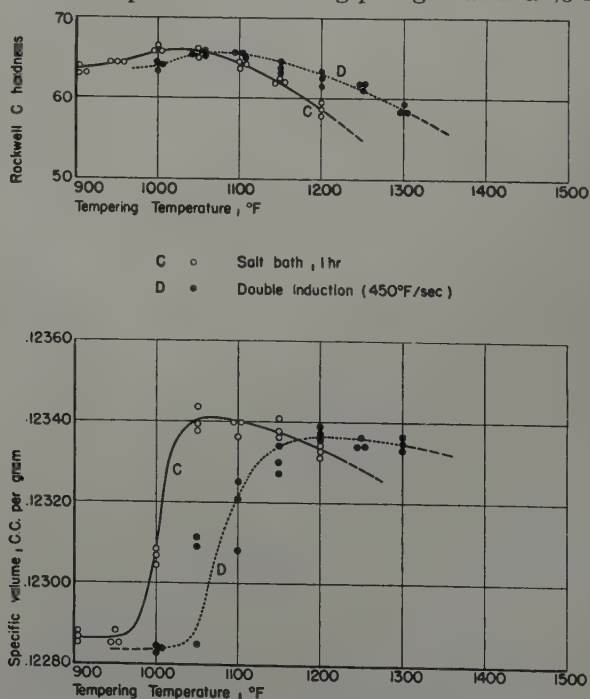


Fig. 3—Hardness and specific volume vs. temperature for various tempering cycles, series C and D.



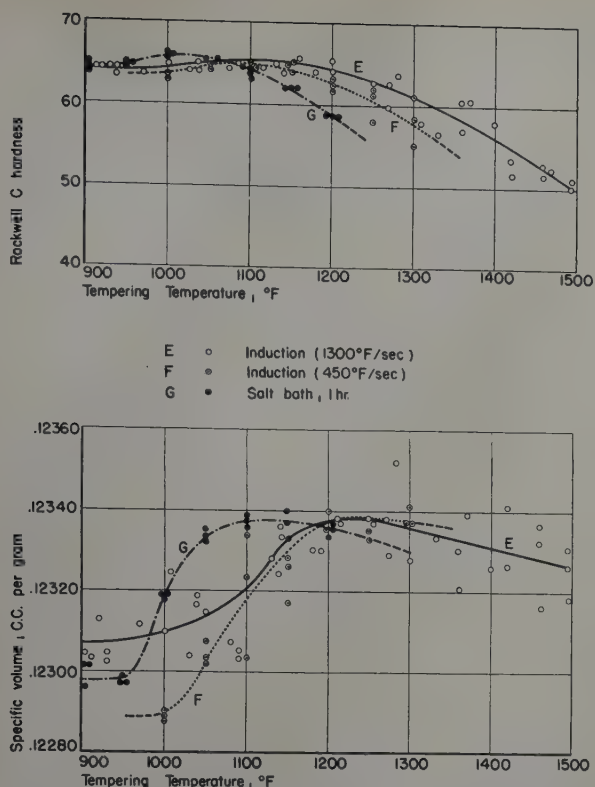


Fig. 4—Hardness and specific volume vs. temperature for various tempering cycles, series E, F, and G.

flat section contacting the specimen, so that upon application of load a 2-point loading system is affected. In comparison with rectangular specimens of similar size, the round specimens have a lower production cost and provide greater plastic deformation. Load deflection curves were constructed from simultaneous readings of load and deflection. From such curves were obtained the proportional limit or stress where the load deflection curve deviates from a straight line and the bend strength or stress at the breaking load.

### Results

**Hardness and Specific Volume:** The hardness and specific volume are plotted as a function of tempering temperature for various tempering treatments in Figs. 2, 3, 4 and 5. The specific volume curves indicate the progress of retained austenite transformation while the hardness curves show the development of secondary hardness. It is interesting to note from the figures that the progress of secondary hardening and retained austenite decomposition is similar for the induction and salt-bath tempered specimens. Essentially the same peak hardness and final specific volume are obtained for all treatments.

In Figs. 6 and 7, the hardness and specific volume data are replotted as a function of the tempering parameter,  $T$  ( $12.5 + \log t$ ). The value of 12.5 for  $c$  was selected after considering the tempering data of Roberts, Grobe, and Moersch<sup>2</sup> for the same type of steel. For comparison, the master tempering curve for hardness obtained by Roberts, Grobe, and Moersch for type 6-5-4-2 high speed steel, hardened at 2175°F (1190°C), is shown in Fig. 6.

The outstanding aspect of the master tempering curves shown in Figs. 6 and 7 is the failure of the curves representing short-time tempering treatments to coincide with the 1-hr tempering treatment. In this connection, it is important to note that the data obtained by tempering for 1 hr in salt (series C) agree reasonably well with the master tempering

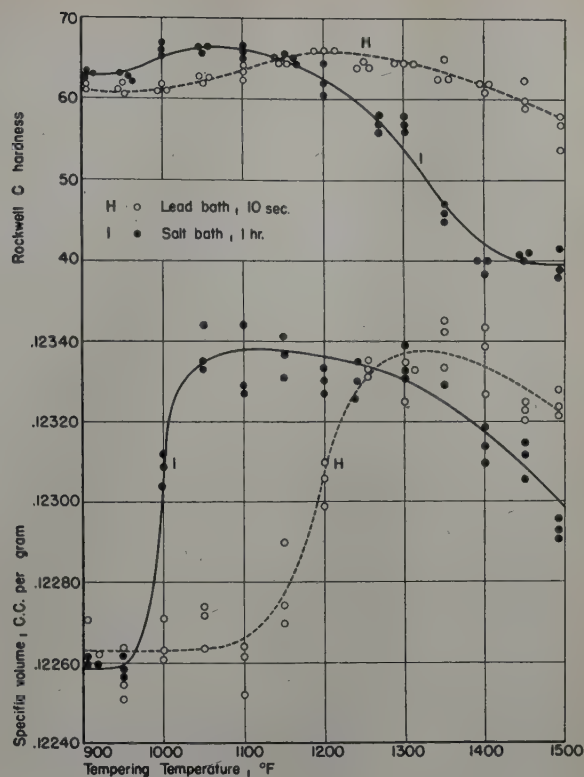


Fig. 5—Hardness and specific volume vs. temperature for various tempering cycles, series H and I.

curve presented by Roberts, Grobe, and Moersch.<sup>2</sup> Whereas previous experimental work has shown that hardness data for a given steel and hardening treatment could be combined into one master tempering curve when plotted against the parameter  $T$  ( $c + \log t$ ), the present experiments indicate that a sizable discrepancy occurs when high speed steel is tempered for a total time of 1 min or less using the rapid heating rates produced by induction heating.

Since the hardness and specific volume curves of the rapidly tempered specimens are displaced to the left of the 1-hr curves, it appears that the short-time tempered specimens have responded to tempering at a rate considerably faster than that predicted by previous work. The acceleration of tempering by the rapid tempering treatments allows a decrease of 170°F (95°C) in the predicted tempering temperature, or a decrease of 240 sec from the predicted tempering time. The acceleration of 240 sec in tempering times compares with an effective tempering time of about 8 sec. This acceleration is of considerable magnitude.

**Physical Properties:** The variation in bend strength and in the proportional limit with tempering temperature for several tempering treatments is summarized in Figs. 8, 9 and 10.

In general, short-time tempering treatments appear to yield bend strength properties which are similar to those produced by the 1-hr treatment. Analysis of bend test results and the hardness and specific volume data, presented in Figs. 2, 3, 4 and 5, indicates that the maximum bend strength occurs approximately 100°F (55°C) above the temperature for maximum secondary hardness and coincides approximately with the tempering temperature providing maximum specific volume in all instances except that of double tempering by induction. It has been found by Bishop and Cohen<sup>8</sup> that maximum hot hardness also coincides with the completion of retained austenite transformation. This degree of

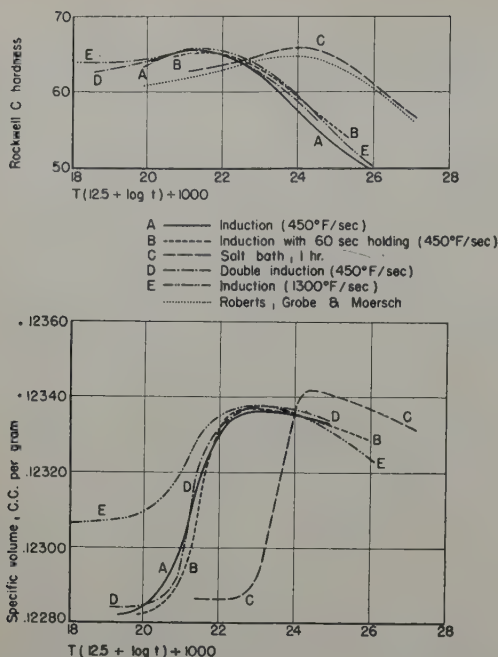


Fig. 6—Hardness and specific volume as a function of the tempering parameter  $T (12.5 + \log t)$ , series A through E.

tempering is usually utilized in practical applications.

The physical properties representing double tempering by induction (series D) show the effect of retempering martensite formed upon cooling from the first tempering treatment. The rather sharp peak in bend strength exhibited by specimens rapidly tempered (series A) is leveled off moderately by the double tempering treatment.

An unusual feature of the bend-test results is the high values of bend strength and proportional limit. Zmeskal<sup>9</sup> has also reported high values of bend strength for round specimens of high speed steel

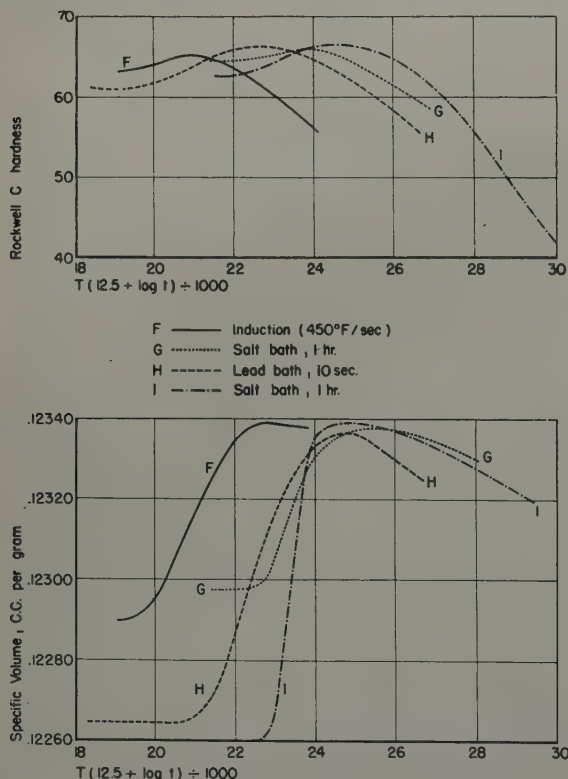


Fig. 7—Hardness and specific volume as a function of the tempering parameter  $T (12.5 + \log t)$ , series F through I.

and has remarked that they are higher than those for rectangular cross-sectioned specimens. It is suggested that this may be due to stress concentration developed at corners of the latter specimens.

An evaluation of the modulus of elasticity was made using the measured values of load and deflection and was found to average  $31.0 \times 10^6 \pm 1 \times 10^6$  psi. This compares with the value of  $32.0 \times 10^6 \pm 0.5 \times 10^6$  psi obtained by Grobe and Roberts<sup>5</sup> for 18-4-1 type high speed steel.

### Discussion

An analysis of the results indicates that W-Mo type high speed steel is capable of successful response to very rapid tempering cycles. Maximum hardness and strength values have been obtained with induction-tempering cycles, which appear similar to those resulting from conventional tempering treatments. As expected, the tempering temperature for maximum hardness and strength is shifted to higher temperatures.

As mentioned previously, however, the tempering reactions appear to be accelerated by induction-tempering treatments to rates considerably greater than those predicted by the parameter  $T (c + \log t)$ . In this connection a number of possible explanations have been considered.

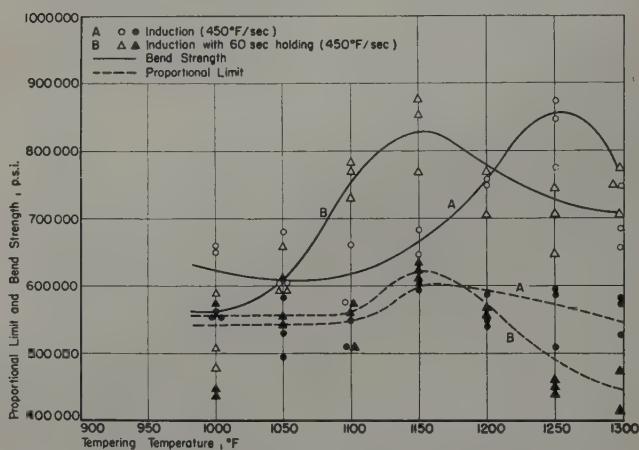


Fig. 8—Influence of various tempering treatments upon bend strength and proportional limit, series A and B.

**Influence of High Frequency Current:** It has been proposed<sup>10</sup> that the very high amperage currents induced in steel heated by induction may accelerate metallurgical reactions by localized heating in the metal. It appears conceivable that such a phenomenon might promote more rapid tempering. To evaluate this supposition, series H of specimens was tempered in a lead bath to maintain a relatively high rate of heating but to eliminate the influence of high frequency current.

The results, plotted in Fig. 7, indicate that induced currents are not responsible for the increased rate of tempering exhibited by the induction-tempered specimens. A comparison of the tempering curves for specimens tempered in lead, series H, and those tempered in salt for 1 hr, series I, shows that the curves still lack coincidence, although to a smaller degree. Since a study of the heating and cooling curves for the specimens heated in lead and by induction (Fig. 1) indicates the primary difference in treatment to be in the heating rate, the discrepancy between the induction and lead-bath heated specimens is attributed to the difference in heating rate as discussed below. It is believed that this result



adds further confirmation to the work of J. G. Kerr,<sup>11</sup> who concluded that induction heating did not accelerate the solution of carbides by localized heating on a microscopic scale.

**Influence of Heating Rate:** The rate of heating appears to provide the most satisfactory explanation for the acceleration in the rate of tempering associated with short-tempering treatments. The specimens tempered by induction are characterized by their rapid rates of heating in addition to the short tempering time. The rate of heating which appears most important is the rate at which the specimen approaches the tempering temperature. In this respect, the specimens tempered in lead exhibit a considerably slower heating rate. It is believed significant that the tempering curve for specimens tempered in lead, employing a heating rate less than that of induction but greater than that in salt, occupies an intermediate position in Fig. 7.

**Theoretical Treatment:** It is proposed that plastic deformation or thermal strain caused by very rapid heating to the tempering temperature is responsible for the deviation of the induction-tempered specimens from the master tempering curve. Such plastic strain is thought to accelerate the tempering reac-

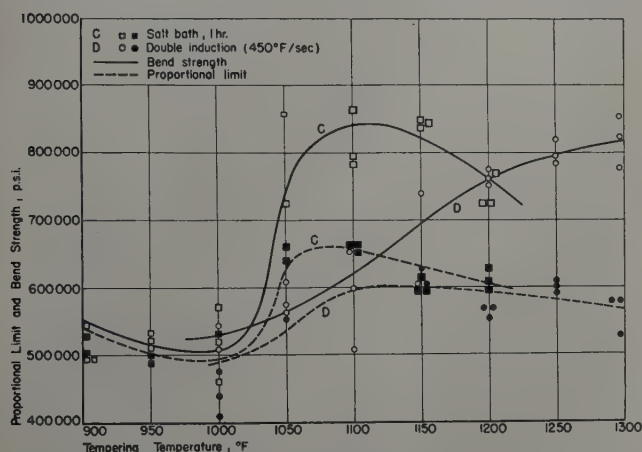


Fig. 9—Influence of various tempering treatments upon bend strength and proportional limit, series C and D.

tions during heating and to place the steel in an advanced state of tempering at the instant the tempering temperature is reached.

This behavior is illustrated in Fig. 11 where an example is given of the progress of tempering in a specimen tempered at 1025°F (550°C). The solid line represents the progress of tempering as a function of the effective tempering time for a tempering treatment, which conforms to the ideal parameter  $T$  ( $c + \log t$ ). The parameter  $P$  in this study is defined as a measure of the actual degree of tempering as represented by hardness and specific volume.

The values of  $P$  experimentally determined for various tempering cycles are plotted in Fig. 11. It will be noted that while the point representing a 1-hr tempering treatment lies on the master tempering curve, the points representing short-time tempering lie considerably above the solid line, as

\* The theoretical value of the tempering parameter at the end of a very rapid heating curve may be calculated by subdividing the curve into smaller and smaller intervals of time and graphically integrating the equation  $P = T \log \left( \frac{\Delta t}{t_0} + 10^{P_0/T} \right)$  interval by

interval from the beginning to the end of the heating curve for each size of the subdivisions. As the intervals become smaller and more numerous, the value of the tempering parameter will approach asymptotically the correct value. As a practical short-cut, only the upper third or fourth of the heating curve may be used for each series of calculations.

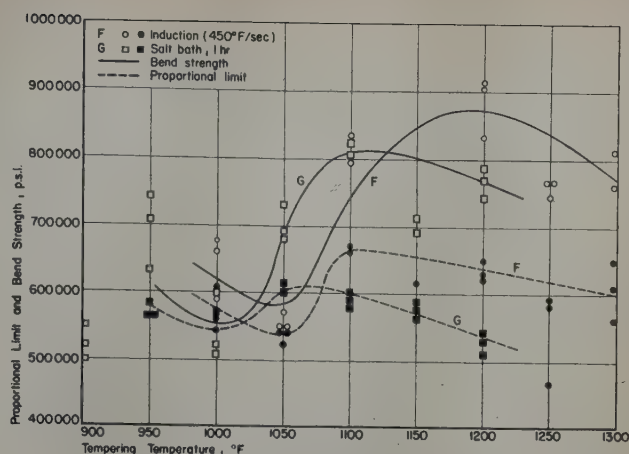


Fig. 10—Influence of various tempering treatments upon bend strength and proportional limit, series F and G.

might be expected since rapid tempering has yielded accelerated results.

The broken curve in Fig. 11 is an application of the equation,  $P = T \log \left( \frac{\Delta t}{t_0} + 10^{P_0/T} \right)$  using the

value of  $P$  for the experimentally obtained 8.8-sec, induction-tempering point as a starting value of  $P_0$ . When the curve is extended forward by the step-by-step integration method, it gradually merges into the master tempering curve. Extending the broken curve to shorter times reveals the interesting inference that specimens induction tempered at 1025°F (550°C) reached the tempering temperature with an initial value for  $P$  of approximately 22,500. This value represents an advanced state of tempering which will not significantly further progress until approximately 60 sec have elapsed. The calculated value of the tempering parameter for the induction-tempered specimen (heating rate equals 450°F per sec) at the instant it attains the tempering temperature was determined from a recorded heating curve to be only 17,500.\*

**Influence of Plastic Strain:** The suggested cause for the initially advanced state of tempering at the instant the steel reaches the tempering temperature after very rapid heating is that rapid heating rates introduce plastic strains which accelerate the tempering reactions.

Two principal processes occur during the tempering of high speed steel: 1—the nucleation and growth of carbides, and 2—the conditioning of the retained austenite for its subsequent transformation upon cooling to room temperature. Averbach<sup>12</sup> has

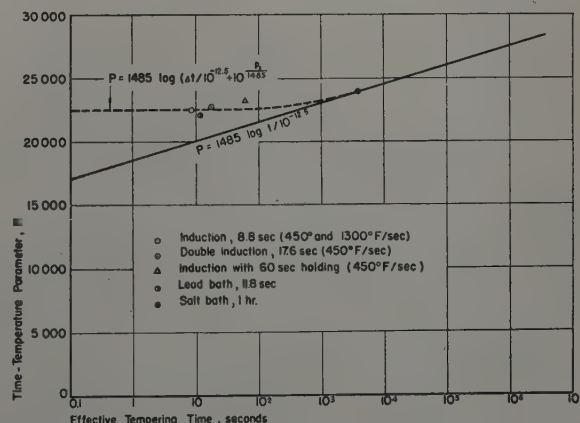


Fig. 11—Experimental and theoretical variation of tempering parameter  $P$  with effective tempering time at 1025°F.

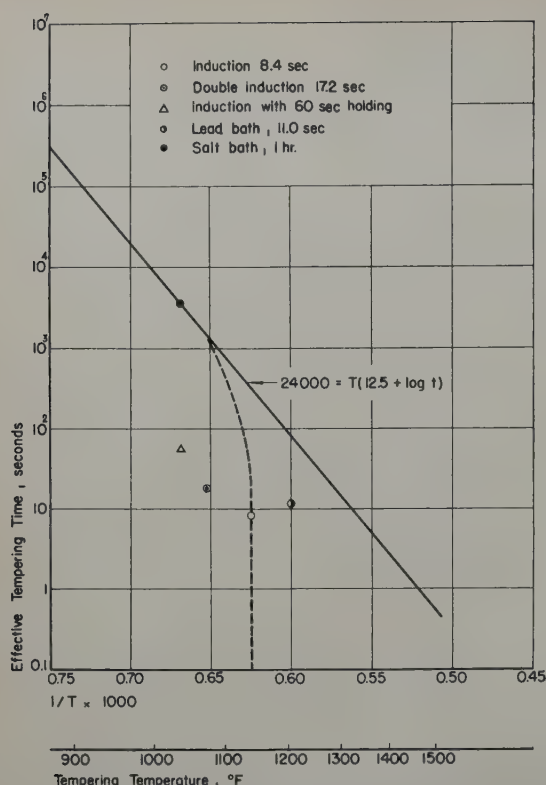


Fig. 12—Log effective tempering time vs.  $1/T$  for high speed steel given various tempering treatments.

given a literature review of the effect of plastic deformation on diffusion reactions, i.e., those reactions which proceed by the mechanism of nucleation and growth. It was found that the velocity of aging processes is invariably increased by plastic strain after solution heat treatment, but not by elastic strains. This is thought to be due principally to the increased rate of nucleation along the slip planes.

Nabarro,<sup>18</sup> discussing the relation of strain, diffusion, and precipitation, cites a number of references which conclude that plastic strain accelerates nucleation and growth processes. Of particular interest perhaps is an indication that diffusion may be very rapid while plastic deformation is actually in progress. Such a condition may prevail when specimens are heated with extreme rapidity to the tempering temperature by induction.

It should be understood that the plastic strain must be present during the nucleation and growth processes. If such a process takes place above the temperature of recovery and recrystallization, any prior strains will be largely removed by the time the heat-treating temperature is reached. For this reason the work of Fisher and MacGregor<sup>14</sup> hardly proves their contention that "the rate of tempering does not change in the presence of strain." Further, the results of the present work disagree with their statement that "the tempering parameter  $P$  uniquely fixes the degree of tempering . . . even when tempering proceeds in the presence of . . . strain, strain rate and stress." When plastic strain is present during tempering, it is believed the tempering reactions will be accelerated. If plastic straining occurs during the heating part of the tempering cycle, then the tempering reactions may be accelerated to an advanced state by the time the tempering temperature is reached. If an aging process occurs below the recrystallization temperature, as in many age-hardening alloys, then prior strain will mark-

edly influence the rate of aging,<sup>15</sup> since the effect of strain is only slowly dissipated.

That plastic strain immediately above the  $M_s$  point induces transformation of retained austenite is also well known. Averbach, Kulin, and Cohen<sup>16</sup> have found that the rate of the martensite reaction from the austenite is also a function of plastic strain and not of elastic strain. Jepson and Thompson<sup>17</sup> found that a stress of 10 tons per sq in. will approximately double the rate of transformation of austenite to bainite in a plain carbon steel. They noted also that transformation appeared to occur preferentially on planes of maximum shear stress.

Thus it appears from the literature that plastic strain may also accelerate the conditioning process in retained austenite during tempering of high speed steel. If the martensitic reaction is considered a nucleation and shear mechanism,<sup>18,19</sup> it may be reasoned that thermal strain will increase within the retained austenite the number and size of alloy carbides and also the number of the carbide embryo and the number of the martensitic embryo which Cohen, Machlin, and Paranjpe<sup>20</sup> have postulated to be strain embryo or dislocations.

Returning again to Fig. 11, it can be seen that the induction-tempering treatments with both heating rates of 450° and 1300°F (250° and 720°C) per sec produce about the same deviation from the ideal curve. Apparently these two heating rates produce similar accelerating effects.

The dashed curve in Fig. 11 represents the course of tempering with time which a steel should take as it is held exactly at 1025°F (550°C) after attaining the initially advanced state of tempering of  $P = 22,500$ . The point representing the double induction-tempering treatment lies slightly above this line, suggesting that the double heatings accelerated the tempering reactions to a slightly greater extent than the single heating. The point representing the 60-sec tempering treatment shows the greatest deviation from the dashed line. It appears that accelerated tempering took place during the 60 sec at temperature. Actually, specimens of this series were held at temperature by oscillating  $\pm 15^\circ\text{F}$  ( $8^\circ\text{C}$ ) about the tempering temperature for a total of about 20 times. It is thought that the power impulses produced enough thermal strain to advance the state of tempering from that represented by the single induction-tempering point to that of the 60-sec point. The point representing the lead-bath tempering treatment lies below the dashed curve as can be expected, since the final heating rate was considerably less than the heating rates for induction heating.

In the absence of the effect of thermal straining, the double-induction treatments and the 60-sec treatments should produce no significant advancement of the state of tempering over that produced by the single-induction treatment; however, the double-induction and 60-sec curves in Figs. 2 and 3 illustrate again the magnitude of the acceleration by their displacement from the curves representing single-induction tempering.

**Maximum Secondary Hardness:** Fig. 12 is a plot of  $\log t$  vs.  $1/T$  for the state of maximum secondary hardness. The solid straight line is the master tempering curve for the peak hardness and the points show the actual time and temperature experimentally found to attain peak hardness for various tempering cycles. The dashed curve is drawn to show the probable experimental relation between time and temperature for specimens which are heated



rapidly by induction and held steadily for the proper lengths of time to yield maximum secondary hardness. It is, in other words, the locus of time-temperature points for maximum secondary hardness in specimens heated rapidly by induction and held at temperature without oscillation. It can be seen that, under such conditions of heating, maximum secondary hardness should not occur at above 1150°F (620°C), regardless of the tempering time. It is important to note that the maximum secondary hardness for the 60-sec induction treatment and the double-induction treatment requires temperatures considerably less than the single-induction treatment. It is interesting to notice also that maximum secondary hardness, for a 60-sec oscillating cycle, occurs at about the same temperature as it does for the 1-hr salt-bath treatment.

Examination of Figs. 2 to 5 shows that there is a slight difference in orientation between the hardness curves and the specific volume curves when the induction-tempering curves are compared with the 1-hr curves. The relative positions of the specific volume curves with respect to the hardness curves in Figs. 2 to 5 indicate that the effect of induction-heating treatments in accelerating the transformation of retained austenite is slightly less than in the development of secondary hardness. This may indicate that the effect of thermal strain is slightly less in the transformation of retained austenite than in nucleation and growth of carbides.

The magnitude of the maximum secondary hardness for the induction-tempered specimens was found to be about one-half point Rockwell C below that of the specimens tempered 1 hr. This may be due to a greater amount of retained austenite in the induction-tempered specimens.

### Summary

1—Rapid induction tempering of W-Mo high speed steel produces mechanical properties, as indicated by hardness and bend test results, which are approximately equal to those resulting from conventional long-time tempering treatments.

2—Short-time tempering data for high speed steel exhibits a lack of conformance to the tempering parameter  $T(c + \log t)$ . It appears that tempering reactions are accelerated by rapid induction tempering to rates considerably greater than those predicted by the parameter. Plastic deformation or thermal strain during the heating part of the short tempering cycle is thought to be the cause of the tempering anomaly. It is believed that such strain accelerates the tempering reactions during rapid heating so as to place the steel in an advanced state of tempering at the instant the tempering temperature is reached. This advanced state will not proceed significantly until after a period of time depending on the extent of advancement. Induction-tempered, high speed steel which is held at the tempering temperature by short power impulses is found to undergo additional acceleration of the tempering reactions during the holding period. This is thought to be due to small thermal strain produced by the temperature oscillations. By this method of tempering maximum secondary hardness may be reached in at least a few minutes at a temperature which would normally require 1 hr by conventional methods.

3—At maximum secondary hardness, high speed steel which is induction tempered by rapid heating exhibits a slightly greater proportion of retained

austenite than does the steel which is conventionally tempered for long times.

4—Maximum bend strength for high speed steel whether tempered rapidly by induction or slowly by salt bath approximately coincides with the completion of the retained austenite transformation.

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# Intermediate Phases in Ternary Alloy Systems Of Transition Elements

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The 1200°C isothermal sections of the following ternary phase diagrams were investigated: Cr-Co-Ni, Cr-Co-Fe, Cr-Co-Mo, and Cr-Ni-Mo. In all these systems the  $\sigma$  phase was found to form extended solid solutions. Two new ternary phases of unknown structure were identified. The existence range of intermediate phases of transition elements was correlated with 3d electron vacancy concentrations.

THE occurrence of extensive ternary  $\sigma$  solid solutions in the Cr-Co-Ni and in the Cr-Co-Fe systems was described in a brief note.<sup>1</sup> More recently  $\sigma$  solid solutions were also found in the Cr-Fe-Mo system by two independent groups of investigators.<sup>2,3</sup> The existence of binary  $\sigma$  phases in the V-Co and V-Ni systems, predicted in ref. 1, was experimentally discovered recently by Duwez and Baen<sup>4</sup> and independently by W. B. Pearson, J. W. Christian, and W. Hume-Rothery.<sup>5</sup> Duwez and Baen stated two general conditions for the occurrence of the  $\sigma$  phase in alloys of the transition elements: "(1) The atomic diameters of the two metals do not differ by more than 8 per cent. (2) One of the two metals has a body-centered cubic structure while the other is face-centered cubic, at least in one of its allotropic forms."

In the course of an extensive research program conducted at this Laboratory under the sponsorship of the NACA, several ternary systems, containing  $\sigma$  solid solutions and also certain new ternary phases, were investigated. The present report describes the investigated portions of the 1200°C isothermal sections of the following ternary phase diagrams: Cr-

Co-Ni, Cr-Co-Fe, Cr-Co-Mo, and Cr-Ni-Mo. It was found that the range of existence of the  $\sigma$  phase in these four ternary systems, as well as in one of two ternary systems which were investigated by others, can be fairly consistently described in terms of electron vacancy concentrations. This supports the suggestion of Sully and Heal<sup>6</sup> that the  $\sigma$  phase is an electron compound.

## Experimental Procedure

The ternary alloys were prepared by vacuum induction melting in zirconia and alumina crucibles. Lot analyses of the metals used are given in Table I.

Specimens of all alloys were annealed at 1200°C in an atmosphere of purified 92 pct helium and 8 pct hydrogen mixture. Alloys consisting mainly of

Table I. Lot Analyses by Weight Percent

| Element<br>or<br>Compound | Cobalt<br>Ronde-<br>lles | Chro-<br>mium | Electro-<br>lytic<br>Iron<br>(H <sub>2</sub><br>Anneal) | Nickel  | Molyb-<br>denum |
|---------------------------|--------------------------|---------------|---------------------------------------------------------|---------|-----------------|
| C                         | 0.17                     | 0.01          | 0.010                                                   |         | 0.003 max.      |
| CaO                       | 0.12                     |               |                                                         |         |                 |
| Co                        | Balance                  |               |                                                         | 0.6-0.8 |                 |
| Cr                        |                          | Balance       | <0.015                                                  |         |                 |
| Cu                        | 0.02                     | Trace         | <0.03                                                   | 0.01    |                 |
| Fe                        | 0.12                     | 0.06          | Balance                                                 | 0.01    | 0.005 max.      |
| H <sub>2</sub>            |                          | 0.045         |                                                         |         |                 |
| MgO                       | 0.04                     |               |                                                         |         |                 |
| Mn                        | 0.06                     |               | <0.01                                                   |         |                 |
| Mo                        |                          |               | <0.015                                                  |         |                 |
| N <sub>2</sub>            |                          | 0.10          |                                                         |         |                 |
| Ni                        | 0.46                     |               | <0.03                                                   | Balance |                 |
| O <sub>2</sub>            |                          | 0.51          |                                                         |         | 0.003 approx.   |
| P                         |                          |               | 0.003                                                   |         |                 |
| Pb                        |                          | 0.001         |                                                         |         |                 |
| S                         | 0.009                    | 0.012         | 0.002                                                   | 0.001   |                 |
| Si                        |                          |               |                                                         |         |                 |
| SiO <sub>2</sub>          | 0.13                     |               | <0.03                                                   |         |                 |

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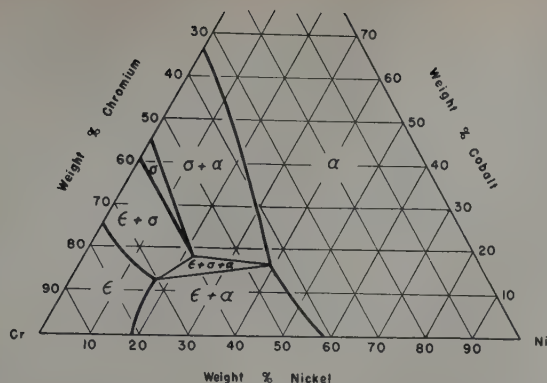


Fig. 1—Isothermal section at 1200°C of the Cr-Co-Ni ternary phase diagram. Alpha phase is face-centered cubic. Epsilon phase is body-centered cubic. Sigma has a complex tetragonal structure.

the face-centered cubic  $\alpha$  phase were double-forged, with intermediate annealing. The double-forged specimens were final annealed for 90 hr at 1200°C and then quenched in cold water. Alloys containing appreciable amounts of any of the other phases could not be forged. Such specimens were annealed for 150 hr at 1200°C and then quenched in cold water. Microscopic specimens of all alloys were prepared by mechanical polishing, in many cases followed by electrolytic polishing. Details of the electrolytic polishing and of the etching procedures used are being published in three NACA Technical Reports, which will also tabulate the intended compositions of the large number of alloys prepared. Many of the alloys were analyzed chemically and, in general, the results are in excellent agreement with the intended compositions.

X-ray diffraction specimens were prepared by filing or crushing the homogenized alloys, and by reannealing the obtained powders in evacuated and sealed quartz tubes. After annealing for 30 min at 1200°C, the tubes were quenched into cold water. X-ray diffraction patterns were made with unfiltered chromium radiation at 30 kv, using an asymmetrical focusing camera of high dispersion. X-ray diffraction in conjunction with microscopic study was used to identify the phases present in each specimen. The amount of each phase was estimated microscopically. The results were used to construct 1200°C isothermal sections of the various ternary phase diagrams. The accuracy of the location of the phase boundaries determined in this manner is estimated to about  $\pm 1$  pct of each component.

### Results

The results of the experimental work are shown in Figs. 1 to 4. It is seen that the  $\sigma$  phase tends to form narrow, extended fields. In the Cr-Co-Ni, Cr-Co-Mo systems this narrow elongated ternary  $\sigma$  phase field is connected with the binary Cr-Co  $\sigma$  phase. The composition range of the latter at 1200°C was found to be about 58 to 60 pct Cr, that is, shifted toward higher Cr contents in comparison with previously reported values.<sup>7</sup> It is significant that in the Cr-Co-Ni and Cr-Co-Fe systems the  $\sigma$  phase extends in a direction corresponding to approximately constant Cr content, indicating that Ni and Fe are capable of partially replacing Co in forming the  $\sigma$  phase. On the other hand, in the Cr-Co-Mo system the  $\sigma$  phase extends in a direction corresponding to approximately constant Co content. This indicates that molybdenum is replac-

ing chromium in forming the  $\sigma$  phase. It is interesting that in the Cr-Ni-Mo ternary system, Fig. 4, the  $\sigma$  phase occurs as a ternary phase; none of the binary systems involved are known to have a  $\sigma$  phase at any temperature. Here too, molybdenum appears to replace chromium in forming the  $\sigma$  phase.

Some exploratory work was done on the Cr-Co-Fe system at 800°C, a temperature where the Cr-Fe binary  $\sigma$  phase exists. It was found that the  $\sigma$  phase field extends continuously from the Cr-Co binary phase to the Cr-Fe binary phase, straight across the ternary system. Fig. 5 shows the  $\sigma$  phase field in the Cr-Co-Fe system at both 1200°C and 800°C. The analogy of the Cr-Co-Ni and the Cr-Co-Fe systems at 1200°C suggests that in the Cr-Co-Ni system at some temperature lower than 1200°C the  $\sigma$  phase might also extend all the way to the Cr-Ni binary system. The fact that none of the previous investigations of this binary system revealed the existence of the  $\sigma$  phase might then be explained on the basis that in the temperature range in which the hypothetical Cr-Ni binary  $\sigma$  phase is stable the rate of diffusion is so low that no appreciable amounts can form in practical periods of annealing. In the course of the present work, several attempts were made to verify this hypothesis, without success. If such a binary phase exists, it is apparently unstable at 500°C and above.

The hexagonal phase designated by  $\mu$  in Fig. 3 was previously known in the Co-Mo binary system<sup>8</sup> as  $\epsilon$ . The new nomenclature was adopted in order to eliminate confusion with the body-centered cubic  $\epsilon$  phase at the Cr end of the Cr-Co system.<sup>7</sup>

As shown in Figs. 3 and 4, new ternary phases were found in the Cr-Co-Mo and Cr-Ni-Mo systems, designated as R and P respectively. The crystal structure of these phases is not known. Table II gives the computed  $d$  values and the estimated relative intensities of their principal X-ray diffraction lines. Both of these phases are very hard. As judged by its tendency to shatter, the P phase appears to be

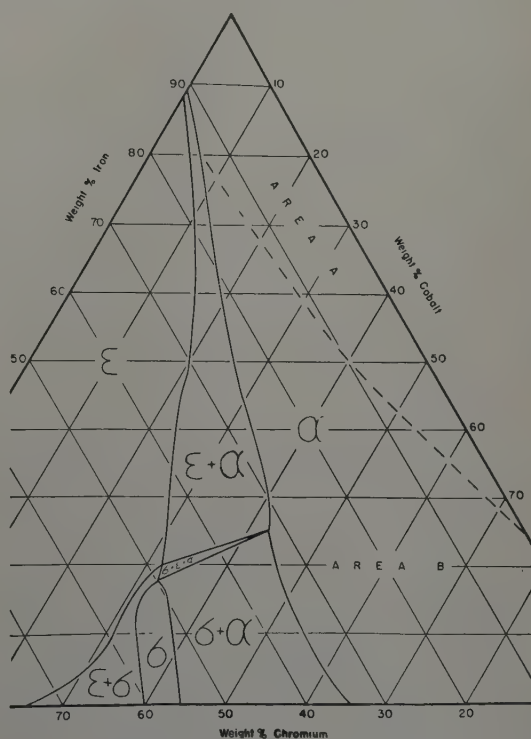


Fig. 2—Isothermal section at 1200°C of the Cr-Co-Fe ternary phase diagram. Phases as in Fig. 1.

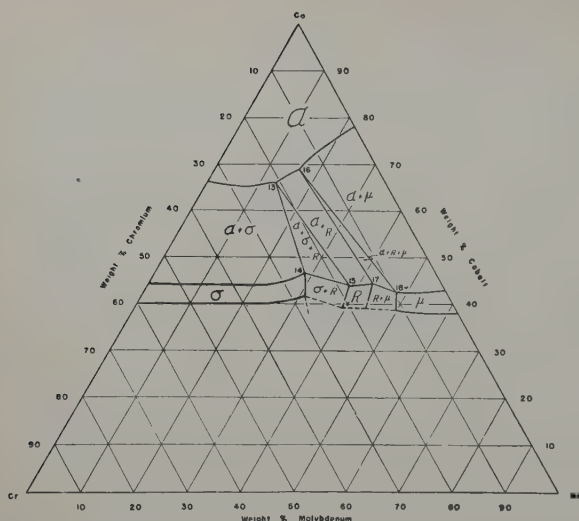


Fig. 3—Isothermal section at 1200°C of a portion of the Cr-Co-Mo ternary phase diagram. The structure of the new ternary R-phase is unknown.

almost as brittle as the  $\sigma$  phase, but the R phase is distinctly less brittle.

Based on Pauling's data for the distribution of valence electrons between cohesive and atomic orbitals in transition elements, a correlation has been found in the above alloy systems between the composition range of the  $\sigma$  phase field and the concentration of electron vacancies in the 3-d subband. Pauling,<sup>9</sup> gives the following numbers for the electron vacancies per atom in the 3-d subband of the various transition elements of the third period: Cr, 4.66; Mn, 3.66; Fe, 2.66; Co, 1.71; and Ni, 0.61.

Assuming that these electron vacancy values are valid for the transition elements in their alloys with each other, the average electron vacancy concentration in single phase alloys of these elements,  $N_v$ , can be calculated according to the following formula:

$$N_v = 4.66(\text{Cr}) + 3.66(\text{Mn}) + 2.66(\text{Fe}) + 1.71(\text{Co}) + 0.61(\text{Ni}) \quad [1]$$

where the symbols (Cr), (Mn), etc., stand for the atomic fractions of the corresponding elements in the alloy.

The electron vacancy concentration in the 4-d subband of molybdenum is not known. Since molybdenum is a transition element following chromium in the same column of the periodic table, it might be assumed that  $N_v$  for the 4-d subband of molybdenum equals that for the 3-d subband of chromium. On this basis, the following formula may be used for molybdenum containing alloys:

$$N_v = 4.66(\text{Cr} + \text{Mo}) + 3.66(\text{Mn}) + 2.66(\text{Fe}) + 1.71(\text{Co}) + 0.61(\text{Ni}) \quad [2]$$

Fig. 6 shows the range of the  $\sigma$  phase field in the 1200°C isothermal sections in the ternary systems studied, and in the systems Cr-Ni-Fe<sup>10</sup> and Cr-Mo-Fe,<sup>2,8</sup> with compositions plotted in atomic percentages. A series of straight and parallel "iso-vacancy" lines (solid lines), each of which represents a constant number of electron vacancies per atom, were also plotted in each diagram on the basis of formula 2.

In the ternary diagrams with molybdenum, better alignment of the elongated  $\sigma$  phase fields with the lines of constant  $N_v$  values may be achieved by assuming a value of  $N_v = 5.6$  for molybdenum. Although such a value has not been suggested on the basis of other evidence, the corresponding "iso-

vacancy" lines were included in the figure (dotted lines in Fig. 6), as calculated from the following formula:

$$N_v = 5.6(\text{Mo}) + 4.66(\text{Cr}) + 3.66(\text{Mn}) + 2.66(\text{Fe}) + 1.71(\text{Co}) + 0.61(\text{Ni}) \quad [3]$$

The composition ranges of the  $\sigma$  phase in the various ternary systems, expressed in terms of concentration of electron vacancies, are given in Table III. For the ternary systems with molybdenum, the composition ranges were calculated on the basis of both formulas 2 and 3, and both sets of values are given in the table.

These results indicate that the  $\sigma$  phase is largely limited to alloys corresponding to the approximate range of 3.36 to 3.6 electron vacancies per atom. A notable exception is the Cr-Fe-Mo system, where the upper limit of the  $N_v$  range is considerably higher. It is not impossible that equilibrium conditions were not attained in the Cr-Fe-Mo system and that the composition range of the  $\sigma$  phase may be narrower than reported. In the Cr-Co-Mo and Cr-Ni-Mo systems the values for the lower limit calculated from formula 2 are distinctly lower than those in other systems. However, better agreement is reached by using formula 3. Although electron vacancy concentrations favorable to the  $\sigma$  phase are in the range of 3.36 to 3.6, it does not follow that all alloys corresponding to this range consist at equilibrium of the  $\sigma$  phase. As postulated by Duwez and Baen, other factors, such as relative atomic size,

Table II. Typical X-ray Diffraction Patterns

| Line No.       | Est. Int.* | $\theta$ | $d$   | Radiation $\text{Cr}_K$ | Line No. | Est. Int.* | $\theta$ | $d$   | Radiation $\text{Cr}_K$ |
|----------------|------------|----------|-------|-------------------------|----------|------------|----------|-------|-------------------------|
| <b>P Phase</b> |            |          |       |                         |          |            |          |       |                         |
| 1              | vw         | 25.54    | 2.650 | $\alpha$                | 25       | mw         | 35.14    | 1.985 | $\alpha$                |
| 2              | vw         | 25.82    | 2.388 | $\beta$                 | 26       | w          | 36.44    | 1.925 | $\alpha$                |
| 3              | vw         | 25.9     | 2.381 | $\beta$                 | 27       | w          | 36.76    | 1.910 | $\alpha$                |
| 4              | vw         | 26.51    | 2.329 | $\beta$                 | 28       | w          | 37.07    | 1.987 | $\alpha$                |
| 5              | w          | 28.35    | 2.191 | $\beta$                 | 29       | vw         | 38.69    | 1.829 | $\alpha$                |
| 6              | mw         | 28.55    | 2.391 | $\alpha$                | 30       | mw         | 60.21    | 1.317 | $\alpha$ 1              |
| 7              | mw         | 28.69    | 2.381 | $\alpha$                | 31       | w          | 60.39    | 1.317 | $\alpha$ 2              |
| 8              | mw         | 29.11    | 2.137 | $\beta$                 | 32       | w          | 60.99    | 1.307 | $\alpha$ 1              |
| 9              | w          | 29.36    | 2.332 | $\alpha$                | 33       | vw         | 61.1     | 1.307 | $\alpha$ 2              |
| 10             | mw         | 29.65    | 2.102 | $\beta$                 | 34       | w          | 61.5     | 1.300 | $\alpha$ 1              |
| 11             | w          | 29.98    | 2.287 | $\alpha$                | 35       | w          | 61.62    | 1.301 | $\alpha$ 2              |
| 12             | w          | 30.21    | 2.067 | $\beta$                 | 36       | w          | 62.71    | 1.285 | $\alpha$ 1              |
| 13             | w          | 30.65    | 2.040 | $\beta$                 | 37       | vw         | 62.88    | 1.286 | $\alpha$ 2              |
| 14             | w          | 30.81    | 2.031 | $\beta$                 | 38       | mw         | 63.48    | 1.277 | $\alpha$                |
| 15             | s          | 31.40    | 2.190 | $\alpha$                | 39       | mw         | 65.06    | 1.260 | $\alpha$ 1              |
| 16             | w          | 31.7     | 2.175 | $\alpha$                | 40       | w          | 65.24    | 1.260 | $\alpha$ 2              |
| 17             | mw         | 32.32    | 2.137 | $\alpha$                | 41       | mw         | 67.34    | 1.238 | $\alpha$ 1              |
| 18             | m          | 32.93    | 2.102 | $\alpha$                | 42       | w          | 67.51    | 1.239 | $\alpha$ 2              |
| 19             | m          | 32.97    | 2.101 | $\alpha$                | 43       | ms         | 73.17    | 1.194 | $\alpha$ 1              |
| 20             | m          | 33.36    | 2.078 | $\alpha$                | 44       | mw         | 73.47    | 1.194 | $\alpha$ 2              |
| 21             | m          | 33.58    | 2.067 | $\alpha$                | 45       | w          | 74.01    | 1.189 | $\alpha$ 1              |
| 22             | mw         | 33.85    | 2.067 | $\alpha$                | 46       | vw         | 74.28    | 1.189 | $\alpha$ 2              |
| 23             | m          | 34.04    | 2.041 | $\alpha$                | 47       | mw         | 76.42    | 1.175 | $\alpha$ 1              |
| 24             | ms         | 34.26    | 2.031 | $\alpha$                | 48       | w          | 76.83    | 1.175 | $\alpha$ 2              |
| <b>R Phase</b> |            |          |       |                         |          |            |          |       |                         |
| 1              | w          | 25.45    | 2.659 | $\alpha$                | 22       | ms         | 35.54    | 1.966 | $\alpha$                |
| 2              | vw         | 25.94    | 2.612 | $\alpha$                | 23       | m          | 35.81    | 1.954 | $\alpha$                |
| 3              | vw         | 26.18    | 2.592 | $\alpha$                | 24       | vw         | 37.22    | 1.890 | $\alpha$                |
| 4              | vw         | 26.43    | 2.336 | $\beta$                 | 25       | w          | 37.42    | 1.881 | $\alpha$                |
| 5              | vw         | 26.87    | 2.529 | $\alpha$                | 26       | vw         | 38.20    | 1.849 | $\alpha$                |
| 6              | w          | 27.52    | 2.473 | $\alpha$                | 27       | mw         | 40.24    | 1.770 | $\alpha$                |
| 7              | mw         | 28.59    | 2.173 | $\beta$                 | 28       | vw         | 62.20    | 1.291 | $\alpha$ 1              |
| 8              | mw         | 28.81    | 2.159 | $\beta$                 | 29       | vw         | 62.22    | 1.293 | $\alpha$ 2              |
| 9              | w          | 29.29    | 2.337 | $\alpha$                | 30       | w          | 63.23    | 1.280 | $\alpha$ 1              |
| 10             | mw         | 29.59    | 2.107 | $\beta$                 | 31       | w          | 63.42    | 1.280 | $\alpha$ 2              |
| 11             | w          | 29.91    | 2.291 | $\alpha$                | 32       | mw         | 64.27    | 1.268 | $\alpha$ 1              |
| 12             | mw         | 30.45    | 2.053 | $\beta$                 | 33       | w          | 64.49    | 1.268 | $\alpha$ 2              |
| 13             | vw         | 30.71    | 2.238 | $\alpha$                | 34       | vw         | 64.81    | 1.263 | $\alpha$                |
| 14             | w          | 31.27    | 2.004 | $\beta$                 | 35       | vw         | 66.51    | 1.246 | $\alpha$ 1              |
| 15             | w          | 31.51    | 2.186 | $\alpha$                | 36       | mw         | 66.69    | 1.246 | $\alpha$ 2              |
| 16             | s          | 31.76    | 2.171 | $\alpha$                | 37       | w          | 68.18    | 1.231 | $\alpha$ 1              |
| 17             | s          | 31.97    | 2.159 | $\alpha$                | 38       | mw         | 68.39    | 1.231 | $\alpha$ 2              |
| 18             | ms         | 32.87    | 2.106 | $\alpha$                | 39       | w          | 69.62    | 1.219 | $\alpha$ 1              |
| 19             | ms         | 33.85    | 2.052 | $\alpha$                | 40       | mw         | 69.90    | 1.219 | $\alpha$ 2              |
| 20             | s          | 34.76    | 2.005 | $\alpha$                | 41       | w          | 71.24    | 1.207 | $\alpha$ 1              |
| 21             | ms         | 35.11    | 1.987 | $\alpha$                | 42       | w          | 71.47    | 1.207 | $\alpha$ 2              |

\* s = strong  
w = weak  
ms = medium strong  
vw = very weak

m = medium  
vw = very very weak  
mw = medium weak



may be decisive in prohibiting the formation of the  $\sigma$  phase in some cases where the above electron vacancy condition is fulfilled.

The electron vacancy concentration ranges for some of the other intermediate phases present in the ternary systems surveyed are also indicated in Fig. 6. These results are summarized in Table IV. It appears that the electron vacancy concentration ranges of the various intermediate phases in the same system may overlap.

Discussion of Results

The observation that nickel, cobalt, and iron, on the one hand, and chromium and molybdenum, on the other, may partially or wholly replace each other in forming the  $\sigma$  phase provides strong additional support for the condition, formulated by Duwez and Baen<sup>4</sup> that the  $\sigma$  phase may be formed when face-centered cubic transition elements are alloyed with body-centered cubic transition elements. From the point of view of the electron vacancy concept, this condition is a result of the requirement for the formation of  $\sigma$  that intermediate electron vacancy concentrations (about 3.36 to 3.6) be attained, between those for the face-centered cubic transition elements Ni, Co, and Fe (0.6 to 2.7) and those for the body-centered cubic transition

Table III. Electron Vacancy Concentration Ranges for the Sigma Phase in Ternary Alloys.

| Ternary System             | N <sub>v</sub> Electron Vacancy Concentration |                           |
|----------------------------|-----------------------------------------------|---------------------------|
|                            | Calculated from Formula 2                     | Calculated from Formula 3 |
| Cr-Co-Ni (1200°C)          | 3.36 - 3.57                                   |                           |
| Cr-Co-Fe (1200°C)          | 3.42 - 3.57                                   |                           |
| Cr-Co-Mo (1200°C)          | 3.18 - 3.57                                   | 3.35 - 3.57               |
| Cr-Ni-Mo (1200°C)          | 3.16 - 3.5                                    | 3.47 - 3.68               |
| Cr-Fe-Ni (650°C)           | 3.51 - 3.66                                   |                           |
| Cr-Fe-Mo (650° and 1300°C) | 3.41 - 4.07                                   | 3.61 - 4.44               |

elements Cr and Mo (4.7 and possibly 5.6). Such intermediate values can be realized in alloys containing both types of transition elements. As seen in Fig. 6, the substitution rules for ternary alloys mentioned may be more sharply formulated in terms of this electron vacancy concentration requirement than in terms of atom for atom substitution of one face-centered (or similarly one body-centered) cubic transition element for another.

Since manganese has an electron vacancy number near the upper limit tolerated in the  $\sigma$  phase, it might be expected that manganese metal itself, or manganese-rich alloys with other transition elements would have favorable electron vacancy conditions to form the  $\sigma$  phase. In fact, A. R. Troiano<sup>11</sup> found that the X-ray diffraction patterns obtained for quenched specimens of a certain Mn-rich Mn-Fe alloy contained lines of the  $\sigma$  phase. It might be also expected that in Cr-Co-Mn and similar ternary systems the  $\sigma$  phase would be able to dissolve considerable quantities of manganese, thus forming extensive solid solution fields. The  $N_v$  values calculated from formula 1 of the present paper for the limits of the Cr-Mn  $\sigma$  phase given by Pearson, Christian, and Hume-Rothery in their recent paper<sup>5</sup> are 3.83 and 3.94. These values are much higher than the upper limit found for the various  $\sigma$  phases investigated in the present paper. In order to bring about agreement, manganese would have to be as-

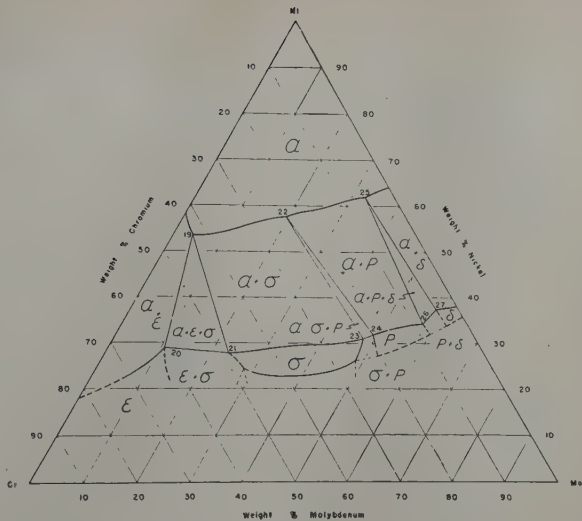


Fig. 4—Isothermal section at 1200°C of a portion of the Cr-Ni-Mo ternary phase diagram. The structure of the new ternary P-phase is unknown.

signed a vacancy number of approximately 3.3 instead of Pauling's value of 3.66. The cause for the anomalous behavior of manganese in these alloys is not well understood.

In the Fe-V system the  $\sigma$  phase appears to extend over a considerable range of composition. The concentration limits at 700°C, as determined by Martens and Duwez<sup>13</sup> are 37 atomic pct and 57 atomic pct of vanadium. If it is assumed that the number of electron vacancies in vanadium is 4.66, as in chromium, the  $N_v$  values for the  $\sigma$  phase boundaries at 700°C are 3.29 and 3.80, respectively. The average value is quite closely the same as that for the range of 3.36 to 3.6, given above for other  $\sigma$  phases. An  $N_v$  value for vanadium similar to that for chromium is strongly suggested by the recent work of Martens and Duwez<sup>13</sup> on the V-Cr-Fe ternary system, where the  $\sigma$  phase forms a continuous series of solid solutions from the V-Fe to the Cr-Fe binary system, with the average atomic percentage of Fe remaining approximately constant from one end to the other of the series. For the recently discovered V-Co, V-Ni, and V-Mn  $\sigma$  phases the compositions given in ref. 5 and the value of  $N_v = 4.66$  for vanadium lead to the following figures:  $N_v = 3.21$  for the V-Co alloy with 50.5 atomic pct vana-

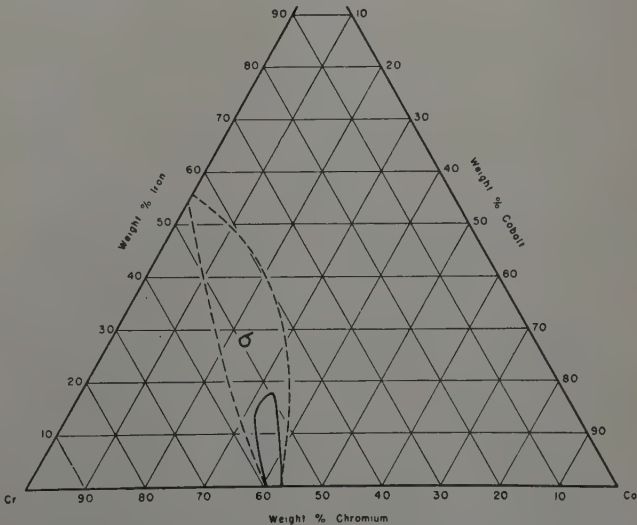


Fig. 5—The sigma phase in the Cr-Co-Fe ternary system at 1200°C (solid lines) and at 800°C (dotted lines).

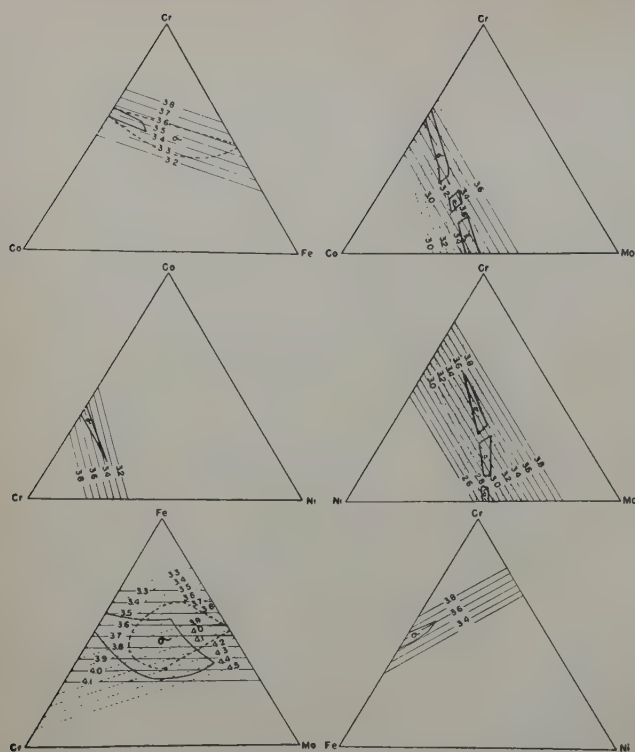


Fig. 6—Survey of intermediate phases in ternary systems of transition elements, plotted in atomic percentage. Systems of straight lines represent constant electron vacancy concentrations, as indicated.

dium, 2.83 to 3.24 for the composition range of 55 to 65 atomic pct vanadium in the V-Ni system, and 3.9 for the V-Mn alloy with 24.3 atomic pct vanadium. The last mentioned figure is too high, and may be brought in line with the usual range by assigning a lower vacancy number to manganese, as suggested in the previous paragraph. Interpretation for the low figures obtained for the V-Co and V-Ni  $\sigma$  phases is at present not available.

After completion of this manuscript, a recent note by A. H. Sully<sup>12</sup> was brought to the attention of the authors. In this publication the correlation of  $\sigma$  phase boundaries with electron concentration in various binary systems is investigated. The results correspond very well with those in the present paper, if it is kept in mind that, under the assumptions made by Sully, the number of excess bonding electrons per atom,  $N_B$ , is related to the number of vacancies per atom,  $N_v$ , as follows:  $N_B = 5.78 - N_v$ . On this basis, the critical value of  $N_B = 2.25$ , found by Sully, corresponds to  $N_v = 3.53$ , which is within the range of 3.36 to 3.60 given in the present paper, and near its upper limit.

### Conclusions

1—In the Cr-Co-Ni, and Cr-Co-Fe phase diagrams at 1200°C the Cr-Co  $\sigma$  phase forms elongated

fields extending deeply into the ternary systems. The extension of the ternary solid solution fields suggests that in these systems nickel, respectively iron is capable of partially replacing cobalt in forming the  $\sigma$  phase. At 800°C the  $\sigma$  solid solution field extends all the way from the Cr-Co  $\sigma$  phase to the Cr-Fe  $\sigma$  phase across the Cr-Co-Fe ternary diagram, so that here Fe and Co are completely replacing each other.

2—In the Cr-Co-Mo system at 1200°C the Cr-Co  $\sigma$  phase forms an elongated field of ternary solid solutions suggesting that molybdenum is capable of partially replacing chromium in forming the  $\sigma$  phase.

3—In the Cr-Ni-Mo system, in which no binary  $\sigma$  phase is known to occur, at 1200°C  $\sigma$  solid solutions form a ternary phase in which chromium and molybdenum may partially replace each other.

4—The above results may be interpreted in terms of electron vacancy concentrations. A condition for the occurrence of the  $\sigma$  phase appears to be the attainment of a range of electron vacancy numbers per atom intermediate between that in the face-centered cubic transition elements, nickel, cobalt, iron, and in the body-centered cubic transition elements, chromium and molybdenum.

5—In the Cr-Co-Mo system a new ternary phase R was found in a small concentration range between the  $\sigma$  and  $\mu$  phases. In the Cr-Ni-Mo system another new ternary phase, P, was located between the  $\sigma$  and  $\delta$  phases. The X-ray diffraction pattern of R is different from that of P, and both patterns appear to be different from those of all known phases in alloys of the transition elements.

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Table IV. Electron Vacancy Concentration Ranges for Some Intermediate Phases

| System   | Phase    | $N_v$ Electron Vacancy Concentration |                           |
|----------|----------|--------------------------------------|---------------------------|
|          |          | Calculated from Formula 2            | Calculated from Formula 3 |
| Cr-Ni-Mo | $\delta$ | 2.65 - 2.84                          | 3.10 - 3.28               |
| Cr-Ni-Mo | P        | 2.88 - 3.34                          | 3.27 - 3.68               |
| Cr-Co-Mo | $\mu$    | 3.05 - 3.28                          | 3.46 - 3.64               |
| Cr-Co-Mo | R        | 3.15 - 3.36                          | 3.41 - 3.62               |



# Oxidation of Titanium

by M. H. Davies and C. E. Birchenall

The rate of oxidation of titanium in the temperature range 650° to 950°C has been measured. The linear rate law obtained is explained by interface reaction control of the process. Tracer experiments indicate the oxygen diffuses in at least one phase of the scale.

THE kinetics of oxidation of titanium, principally at low temperatures and under varying oxygen pressures, have been reported.<sup>1, 2</sup> In the present investigation the rates of oxidation of titanium have been determined by the gravimetric method in the temperature range 650° to 1000°C under 1 atm of oxygen. Some of the scales formed were powdered and an endeavor was made to identify the phases present by X-ray diffraction.

Alexander and Pigeon<sup>1</sup> ascribe a logarithmic rate law to the growth of thick films formed at temperatures up to 565°C, and Gulbransen and Andrew<sup>2</sup> suggest that the parabolic rate law holds up to 600°C. In both cases large initial deviations from those relationships are apparent and no explanation is offered.

In the present experiments it is shown that a linear rate law holds in the temperature range 650° to 1000°C, and it is suggested that the initial deviations observed are due in part to a spurious surface area effect and also to the high solubility of oxygen in titanium metal. Positive information on the mechanism of oxidation is not available, but oxygen ion diffusion through the lattice is inferred from the re-

sults of trace experiments. X-ray analysis of the scale confirms Gulbransen and Hickman's<sup>3</sup> observation on the presence of rutile  $\text{TiO}_2$ .

## Experimental Details

The titanium used in these experiments was prepared by the reduction of titanium tetrachloride with magnesium and was used in the form of rolled sheet. Samples approximately 0.040x0.5x0.75 in. were cut and polished to a fineness of 4/0 on metallographic polishing papers.

Individual samples, suspended on a platinum wire, were lowered into the hot zone of a furnace, in vacuo, by means of a winch, and oxygen was admitted after the desired temperature was attained. The increase of weight of single samples oxidized for fixed times at certain temperatures was determined by weighing the sample before and after oxidation on a chemical balance. In these instances the sample was used for only one time at one temperature. In some cases the course of oxidation was followed by attaching the sample to a sensitive spring balance and noting periodically the extension of the spring with time of oxidation.

Kirkendall type experiments were carried out by marking the surface of the titanium prior to oxidation with a solution containing radioactive silver. After drying, the specimen was heated in vacuo to decompose the silver nitrate used, leaving a small amount of metallic radioactive silver on the surface. Following oxidation, these samples were mounted, ground, and then placed in intimate contact with

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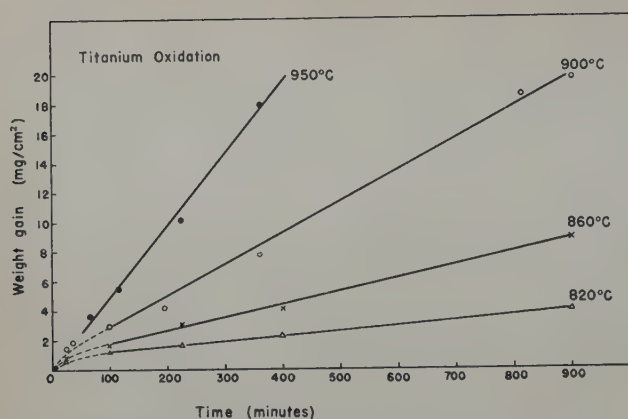


Fig. 1—Isothermal curves showing weight increase with time of titanium oxidized in oxygen between 820° and 950°C.

No-Screen X-ray film for the purpose of obtaining autoradiographs.

High purity electrolytic oxygen was used throughout these experiments to avoid the possibility of nitrogen contamination.

### Experimental Results and Discussion

The rate of gain in weight of titanium oxidized at various temperatures is plotted in Figs. 1 and 2. It can be seen that, apart from initial deviations, the amount of oxygen uptake is a linear function of time.

The reaction rate is expressed by the equation:

$$\frac{W}{A} = lt$$

where  $W$  is the gain in weight of the sample;  $A$ , the area calculated from the geometrical dimensions of the specimen;  $t$ , the time of oxidation, and  $l$ , the proportionality constant. Values of  $l$  at the temperatures studied have been obtained from the linear portions of the various isothermal curves and these are plotted in Fig. 3 as  $\ln l$  vs. the reciprocal of absolute temperature. The values at various temperatures are given in Table I. Several check runs<sup>7</sup> on iodide titanium in the range 900° to 1000°C showed no appreciable differences.

The relative densities of  $\text{TiO}_2$  which forms a considerable part of the scale and titanium metal satisfy the Pilling and Bedworth<sup>4</sup> relationship for the formation of protective scales, and it is thus surprising that a linear rate law should obtain for the oxidation of titanium.

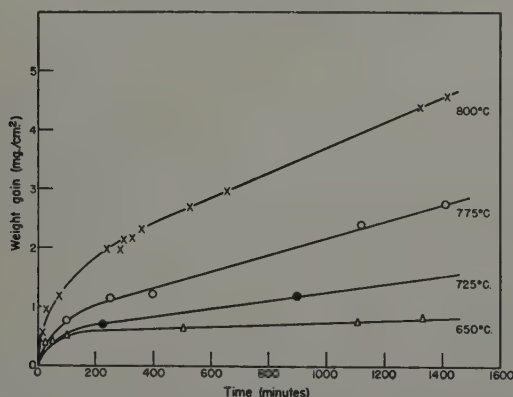


Fig. 2—Rates of titanium oxidation between 650° and 820°C.

The initial deviations from linearity indicated in Fig. 1 are attributable to a surface area effect at least in part; that is, the true surface area exceeds, initially, the surface area calculated from the geometrical dimensions of the specimen by some roughness factor. This effect disappears when the scale attains a minimum finite thickness (which will depend upon the initial surface preparation). Some confirmation of this surface area effect is shown by the value of the  $W/A$ , the weight gain/unit surface area, at zero time obtained from extrapolation of the linear portions of the various curves. This approaches zero as the temperature is raised, Fig. 1.

There is, to the knowledge of the authors, only one other case in the literature of a linear rate law for the oxidation of metals which form a "protective" scale.\* This is for aluminum between 500° and 550°C.<sup>5</sup> Those metals which do conform to a linear rate law are reactive metals such as sodium and magnesium for which the molecular volume of the oxide is less than the molecular volume of the metal.

A complete analysis of the oxidation process with regard to titanium is made unusually complex by the exceedingly high solubility of oxygen in the metal, so that during oxidation a considerable portion of the oxygen uptake enters into solid solution in the metal. This process may contribute also to the initial deviation from linearity. In many cases, complete mechanical separation of metal and scale is possible and in one case (titanium oxidized for 100 min at 900°C) it was found that assuming the scale to be 100 pct  $\text{TiO}_2$ , then 36 pct of the total oxygen entered into solid solution in the metal.

Analysis of a sample oxidized until all metal was consumed yielded the average formula  $\text{Ti}_2\text{O}_3$  and so the value of 36 pct of total oxygen absorbed entering into solid solution is low. Since X-ray analysis of some of the scales has indicated the presence of only  $\text{TiO}_2$ , an average formula of  $\text{Ti}_2\text{O}_3$  can only be explained by the existence of a lower oxide with a wide composition range, since appreciable quantities of a lower oxide of fixed composition would yield a diffraction pattern for the amounts of lower oxide required to give the average composition observed. It is certain that the solubility of oxygen in titanium is high, but detailed information on the Ti-O system is lacking. Ehrlich<sup>6</sup> submits information on the existence of three intermediate phases of lower oxygen concentration than that required for the formation of  $\text{TiO}_2$ . These are in order of increasing oxygen concentration:

| Phase    | Type of Structure | Limits of Composition                   |
|----------|-------------------|-----------------------------------------|
| $\delta$ | NaCl              | $\text{TiO}_{0.6} - \text{TiO}_{1.25}$  |
| $\gamma$ | $\alpha$ Corundum | $\text{TiO}_{1.46} - \text{TiO}_{1.56}$ |
| $\beta$  |                   | $\text{TiO}_{1.7} - \text{TiO}_{1.8}$   |

Rutile,  $\text{TiO}_2$  is ascribed a range in composition from  $\text{TiO}_{1.9}$  to  $\text{TiO}_2$ .

Only one of the above oxides, the  $\delta$  phase, would satisfy the requirements stated previously for a scale of average composition  $\text{Ti}_2\text{O}_3$  whose X-ray diffraction pattern would yield only lines due to  $\text{TiO}_2$ . (A small amount of  $\text{Ti}_2\text{O}_3$  may be present in the scale. Thomas,<sup>7</sup> using more sensitive X-ray techniques, was able to identify the presence of this phase. A lower oxide was also indicated but not identified.)

\* The case of tungsten is not truly analogous since oxides formed on that metal grow out in blocks perpendicular to the surfaces of a parallelepiped specimen. In titanium the oxide is compact and continuous around the metal.



The linear rate law obtained for the oxidation of titanium can be explained on the basis that the process is controlled by some interface reaction, such reaction being of zero order, and it seems most likely that the controlling reaction occurs at the oxide-oxygen interface.

Were the process controlled by the reaction at the metal oxide interface, then it could be expected that the  $\alpha$  to  $\beta$  transformation in the metal would affect the reaction rate. The most recent information<sup>8</sup> on the effect of oxygen on the transition temperature of titanium, which occurs at about 880°C in the pure metal, indicates that the transition temperature is raised by the presence of oxygen in solution. With normal impurities in Kroll titanium, the transformation occurs over the range 860° to 970°C. Any tendency toward lower transformation due to impurities should be counteracted by the oxygen dissolved in the metal. A break in the rate curve, Fig. 3, is obtained at about 830°C, but this cannot be attributed to the phase transformation. Above 830°C  $\ln l$  is another linear function of  $1/T$  with no inflections observed at temperatures up to about 1000°C.

The strong dependence of the rate of oxygen uptake by titanium, during oxidation, on oxygen pressure as found by Gulbransen and Andrew<sup>1</sup> seems to support the theory of interface reaction rate control of the oxidation process. The composition of titanium oxides in equilibrium with varying pressures of oxygen is unlikely to change owing to the apparently very low dissociation pressures of those oxides, and it is thus unlikely that a diffusion controlled process (inferred by a parabolic rate law) would be dependent on oxygen pressure unless that pressure was of the order of the oxygen dissociation pressure of the oxide. On the other hand, it is probable that a surface reaction rate would be sensitive to oxygen pressure.

It can be expected that the plot of  $\ln l$  vs.  $1/T$  for such a surface reaction will yield a straight line and the apparently sharp break in this plot at 830°C cannot be fully explained. A similar occurrence observed in the oxidation of magnesium<sup>10</sup> is associated with the oxidation of that metal in the vapor phase. Oxidation proceeds by the molecular diffusion of oxygen through the oxide and subsequent reaction at the metal-oxide interface. The inflection obtained is attributed to the rapidly increasing vapor pressure of magnesium with temperature and is fully explained in the paper. It is very unlikely that a similar phenomenon obtains in titanium oxidation because of the very low vapor pressure of titanium at these temperatures.

However, a change in color of the outer oxide was noted. Scales formed at 820°C or below exhibited

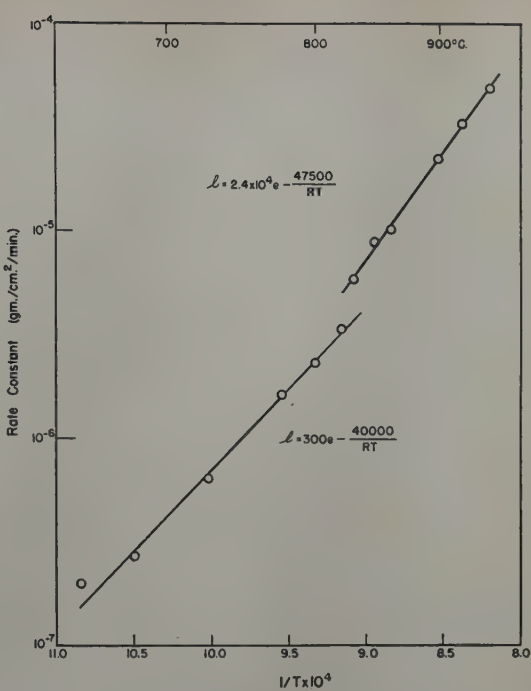


Fig. 3—Plot of the logarithm of  $l$ , the linear rate constant vs. reciprocal of absolute temperature in the oxidation of titanium.

a yellow color on the outer surface whereas those formed above that temperature were orange to brown in color. Although rutile may change its color with changing oxide content, there may be a change in the nature of the outermost oxide resulting in a change in the reaction rate. The change may be due to a phase transformation in the oxide or to the appearance of a new oxide on the surface. The yellow outermost oxide may be  $\text{TiO}_3$ , but scant information is available on this oxide. It is possible that the dissociation pressure of this oxide approaches 1 atm about 830°C and the change in color and reaction rate may be attributable to this effect.

To determine the mechanism of oxidation, attempts were made to follow the movement of inert markers as in experiments by Pfeil,<sup>11</sup> Smigelskas and Kirkendall,<sup>12</sup> and da Silva and Mehl.<sup>13</sup> The marker employed in this case was radioactive silver and the autoradiographic technique was used in the endeavor to locate the marker after oxidation. Since no trace of the radioactive material was obtained, it is presumed that the silver remained at the oxide-oxygen interface and was evaporated during the appreciable times (four days) required to form thick scales at about 900°C. The silver activity employed was high enough that if it had dissolved in the metal and/or oxide, it should have been detected in the Geiger counter measurements which were tried. In similar experiments to determine the diffusing ion involved in the growth of  $\alpha\text{-Fe}_2\text{O}_3$ ,<sup>14</sup> the inert radioactive marker could not be located. Conductivity studies on this oxide confirm that the oxygen ion is mobile in the growth process. The markers in other oxides were located easily when embedded below the surface. During the growth of wüstite on iron<sup>14</sup> the platinum wires on which the samples were hung became enveloped by the growing oxide. This did not occur in the case of titanium oxidation. These results seem to indicate that diffusion of oxygen ions is responsible for the growth process, in at least the outer layer of oxide. That oxygen diffuses in  $\text{TiO}_2$  is suggested by

Table I. Values for  $l$  — the Linear Rate Constant at Various Temperatures

| Temperature,<br>°C | Ti Oxidation<br>1/T Deg. Abs. | $l$ ( = G per<br>Sq Cm per Min) |
|--------------------|-------------------------------|---------------------------------|
| 650                | 10.83x10 <sup>-4</sup>        | 2.0x10 <sup>-7</sup>            |
| 680                | 10.49                         | 2.7x10 <sup>-7</sup>            |
| 725                | 10.02                         | 6.7x10 <sup>-7</sup>            |
| 775                | 9.54                          | 1.65x10 <sup>-6</sup>           |
| 800                | 9.32                          | 2.35x10 <sup>-6</sup>           |
| 820                | 9.15                          | 3.4x10 <sup>-6</sup>            |
| 830                | 9.07                          | 6.0x10 <sup>-6</sup>            |
| 845                | 8.94                          | 8.8x10 <sup>-6</sup>            |
| 860                | 8.83                          | 1.02x10 <sup>-5</sup>           |
| 900                | 8.53                          | 2.25x10 <sup>-5</sup>           |
| 920                | 8.38                          | 3.35x10 <sup>-5</sup>           |
| 950                | 8.18                          | 4.9x10 <sup>-5</sup>            |

the composition limits for that phase given by Ehrlich which show rutile to be an oxygen deficient lattice.

A complete metallographic examination of the scales formed was not possible owing to the extremely brittle nature of the oxides.

### Summary

The results of this investigation and of a previous uncompleted investigation<sup>7</sup> show that titanium oxidized according to a linear rate law, which may be associated with the interface reaction at the oxide-oxygen interface. Slight deviations observed in the behavior of iodide-refined and "Kroll" titanium<sup>2</sup> may be attributable to the presence of impurities, and in particular the presence of hydrogen in titanium produced by the magnesium reduction of TiCl<sub>4</sub> may be responsible for those deviations observed.

The initial nonlinear relationship between oxygen uptake and time of oxidation is attributed to a spurious surface area effect and to the high solubility of oxygen in titanium metal. Rates of oxidation of titanium at various temperatures have been calculated and a reason for the inflection in the plot of  $\ln l$  vs.  $1/T$  postulated.

Experiments to determine the mechanism of oxidation indicate that the diffusion of oxide ions is involved in at least part of the scale.

It is suggested that further work on the oxidation of titanium should be preceded by accurate determination of the Ti-O phase diagram. Subsequent use of refined techniques to evaluate the nature and relative amount of the various phases in the scale should enable the calculation of data relative to their rates of formation and also to the diffusion of oxygen in the metal. In the light of the present experiments, it is unlikely that the diffusion data of Alexander and Pigeon<sup>1</sup> can be very accurate, since it seems that the simultaneous occurrence of an increase in thickness of the film and diffusion of oxygen into the metal does not permit a separation of the numbers

relative to each process from the experimental results available.

### Acknowledgments

This work was sponsored by the Office of Naval Research, whose financial assistance and permission to publish is gratefully acknowledged. The titanium was supplied by the Remington Arms Co., to whom the authors express their thanks. The radioactive silver was obtained from the Isotopes Div., U. S. Atomic Energy Commission. One of us is indebted to the Economic Cooperation Administration for a Fellowship Award. The authors also wish to express their appreciation for the helpful advice and continued interest of M. T. Simnad and R. F. Mehl.

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- <sup>14</sup> M. H. Davies, M. T. Simnad, and C. E. Birchenall: This issue, p. 889.

### Correction

In the January 1951 issue, p. 64, TN 50E, *Crystallographic Angles for Magnesium, Zinc and Cadmium* by Edward I. Salkovitz: Table I contains errors in the crystallographic angles which have been pointed out by J. F. Nicholas, of the Division of Tribophysics, Commonwealth Scientific and Industrial Research Organization, University of Melbourne, Carlton, Vic., Australia. In transmitting the corrections, he commented as follows:

The accompanying table lists the corrected angles where the discrepancy is 0.2' or more. The  $c/a$  ratios used in the technical note and in the corrections are the generally accepted values measured by Jette and Foote<sup>2</sup> on very pure metals at a temperature of 25°C, but do not always agree with the values of  $c$  and  $a$  given in *Metals Handbook*, 1948 edition. An increase in the  $c/a$  ratios of at most 0.0002 will increase the angles for (HKIL) = (0001) by 0.1'.

<sup>2</sup> E. R. Jette and F. Foote: *Journal of Chemical Physics* (1935) **3**, p. 605.

Such increases can be caused by temperature rises of approximately 90°, 2°, and 3°C for magnesium, zinc, and cadmium, respectively, or by small amounts of impurity.

Corrected Values for Table I

| HKIL | hkil           | Magnesium<br>( $c/a=1.6235$ ) | Zinc<br>( $c/a=1.8563$ ) | Cadmium<br>( $c/a=1.8859$ ) |
|------|----------------|-------------------------------|--------------------------|-----------------------------|
| 0001 | 10 $\bar{1}$ 6 | 17° 21.1'                     |                          |                             |
|      | 10 $\bar{1}$ 4 |                               | 28° 11.1'                |                             |
|      | 20 $\bar{2}$ 5 | 36° 51.9'                     | 40° 36.6'                |                             |
|      | 20 $\bar{2}$ 3 |                               |                          | 55° 26.4'                   |
|      | 10 $\bar{1}$ 1 | 61° 55.4'                     |                          |                             |
|      | 21 $\bar{3}$ 2 |                               | 70° 34.4'                |                             |
|      | 21 $\bar{3}$ 1 | 78° 36.0'                     | 80° 0.0'                 |                             |
|      | 11 $\bar{2}$ 4 |                               | 42° 52.0'                |                             |
|      | 12 $\bar{3}$ 2 |                               | 70° 34.4'                |                             |
|      | 12 $\bar{3}$ 1 | 78° 36.0'                     | 80° 0.0'                 |                             |



# Systems Titanium-Molybdenum and Titanium-Columbium

by M. Hansen, E. L. Kamen, H. D. Kessler,

and D. J. McPherson

The highly reactive Ti-Mo and Ti-Cb alloys were prepared and heat treated under protective conditions. Phase diagrams were established based on micrographic and X-ray diffraction analysis and detection of incipient melting.  $\beta$  titanium forms a continuous series of solid solutions with both molybdenum and columbium, whereas these metals are only slightly soluble in the  $\alpha$  titanium modification.

**P**REVIOUS work on the Ti-Mo and Ti-Cb systems was very limited and is discussed in succeeding sections of this paper relating to the respective phase diagrams. The diagrams in the present work were determined principally by micrographic analysis, because other methods such as thermal analysis and dilatometry are not suitable, due to the low diffusion rates of these alloys in the transformation range. X-ray analysis was believed less useful than micrographic analysis because: 1—On quenching certain high titanium alloys from above their transformation range, the body-centered cubic  $\beta$  phase decomposes into acicular  $\alpha$  (hexagonal close-packed) which room temperature X-ray diffraction techniques cannot differentiate from isothermal  $\alpha$ . 2—High temperature X-ray techniques might be used, but are difficult to apply and are subject to error because of the high reactivity of titanium with gases such as oxygen and nitrogen. Although metallographic study was the basic method used, X-ray diffraction analysis was applied to a limited extent, to further substantiate the findings.

The transformation ranges on the titanium side of the Ti-Cb and Ti-Mo systems were studied both with DuPont Process A (magnesium-reduced) titanium alloys and with iodide titanium alloys. The Process A metal was used chiefly to bracket the transformation range in order to reduce the number of alloys given a particular treatment for the more accurate final study with iodide titanium alloys.

## Experimental Procedure

The analyses of the metals used in the preparation of alloys for this study are presented in Table I.

**Melting Practice:** Early in the work, a consumable electrode, arc melting furnace was used in the preparation of the Process A Ti-base Mo and Cb alloys. This type of furnace has been described by other investigators.<sup>1, 2</sup> One of the major difficulties of the consumable electrode melting process was the preparation of homogeneous electrodes (with the mixture of coarse titanium sponge and fine powder alloying addition) which would give homogeneous ingots. Composition gradients encountered may have been due to a tendency for powdered alloying metals to drop away from the electrode in handling. This difficulty in the preparation of homogeneous alloys was overcome by the use of a nonconsumable electrode furnace for later work.

This furnace is similar to the one used by McPherson and Fontana<sup>3</sup> at Ohio State University. A diagram of the nonconsumable electrode arc furnace is given elsewhere.<sup>4</sup> The source of power was a 400 amp dc welding generator.

Electrode tips of tungsten ( $\frac{1}{2}$  in. in diam) were used for all columbium melts and for a limited number of molybdenum melts. Molybdenum tips were used for the majority of molybdenum alloy melts. Columbium tipped electrodes were tried, but disintegrated rapidly at currents above 300 amp.

In the Process A titanium melting practice the metals were charged into the water-cooled spun copper crucible in the following forms: 1—titanium: sponge ( $-4+16$  mesh); 2—molybdenum: sections of 0.003 in. sheet (approximately  $\frac{1}{2}$  in. sq); and 3—columbium: powder compacts ( $\frac{1}{8}$  in. lumps broken from large section). After alternately evacuating and purging the furnace several times with argon or helium, the arc was struck against the metal charge,

M. HANSEN, Member AIME, is Assistant Chairman, and H. D. KESSLER and D. J. McPHERSON are Research Metallurgists, Metals Research Dept., Armour Research Foundation of Illinois Institute of Technology, Chicago. E. L. KAMEN is Lieutenant Junior Grade, U. S. Navy.

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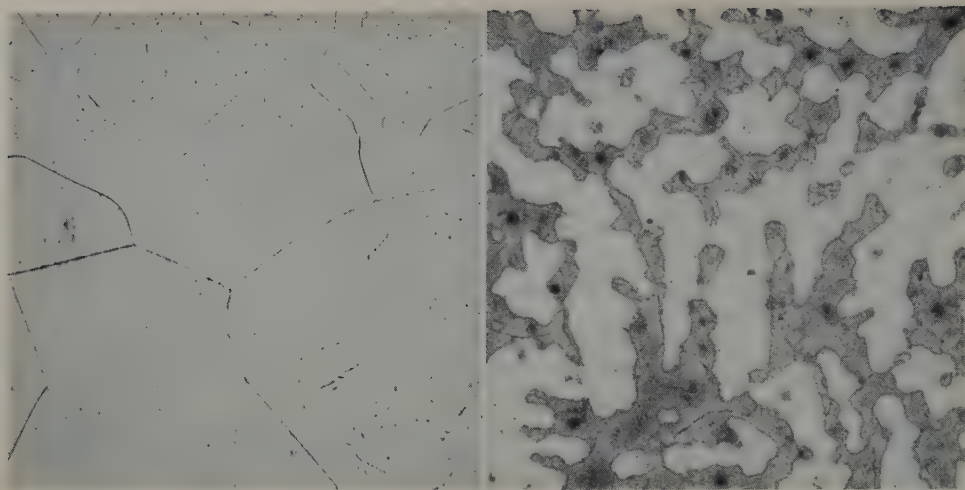


Fig. 1 (left)—A 50 pct Process A Ti-Mo alloy cast and homogenized at 1250°C for 20 hr. Etchant, 1 pct HF, 3 pct HNO<sub>3</sub> in water. X250.

Fig. 2 (right)—Same alloy as Fig. 1, but without homogenization treatment.

which weighed 50 to 100 g. In general, 300 amp was applied for about 2 min, until most of the material in the crucible was melted. The current then was raised to 600 amp, and the arc so directed as to blast through the melt over the entire area covered by the molten metal. Using this blasting technique, only one or two remelts had to be made to produce a homogeneous ingot.

The iodide titanium alloy melting practice was similar to that used for Process A titanium, with the addition of several refinements. The major change for iodide titanium alloys was the adoption of a copper block crucible insert. As iodide melts ranged in size from 5 to 30 g, a smaller melting cavity was desired. Adjacent to the cavity was a tungsten insert, projecting above the level of the surface of the block. The arc was struck against the tungsten insert and then was carried over to the charge in the block cavity. With this technique, the electrode never contacted the charge and, thus, a possible source of contamination was eliminated. The iodide titanium was charged in the form of small sections cut from 1/16 in. sheet obtained by cold rolling hairpin bars.

All columbium and molybdenum alloys were

melted at least three times to achieve homogeneity. To avoid reopening the furnace and purging it, a rod was used to invert the ingot after each remelting operation. Complete dissolution of the high melting columbium and molybdenum additions in the melt was insured by radiographic inspection of samples. Helium gas at atmospheric pressure was used for all iodide melts and little or no hardness increase was obtained during the melting process.

When melting on the copper block, the current was never raised above 350 amp, as higher currents were found to cause the molten titanium alloys to wet the copper. Arc voltages of 30 to 35 v gave satisfactory arc lengths for most melting work in helium. Tungsten pickup from the tungsten tipped electrodes was generally less than 0.10 pct.

**Annealing Treatments:** Early in this investigation, it was decided to anneal all specimens in evacuated Vycor bulbs rather than in inert atmospheres, where oxygen and nitrogen contamination could possibly occur during long heat treatments. It was found that  $\beta$  solid solution samples annealed in argon were characterized by a surface layer containing  $\alpha$  phase stabilized by oxygen and/or nitrogen, whereas no contamination took place in the Vycor bulb.

In order to prevent collapse of Vycor bulbs during treatments at 1000° to 1150°C a reduced pressure of argon was admitted to the bulbs at room temperature. The argon pressure was regulated so that it would balance one atmosphere at the temperature of treatment. The alloys were quenched after heat treating by breaking the Vycor bulb under the surface of cold water to allow direct cooling of the specimens.

One of the first steps in the annealing program was the determination of the optimum treatment to bring the alloys toward equilibrium at the various temperature levels. A program was undertaken to show the effects of increased annealing times, cold work, and repeated cold work-annealing cycles upon the structures of alloys. The results of this program indicated which of the several treatments undertaken appeared to achieve equilibrium conditions for the various alloys. As a factor of safety, cold work prior to the isothermal anneal and substantially longer annealing times than those determined in the above program were employed. The furnace temperature control was within  $\pm 5^\circ\text{C}$  of the reported temperatures.

**Homogenization:** Certain of the high Ti-Cb and Ti-Mo alloys showed coring even after hot forging and annealing treatments. Therefore, it was found

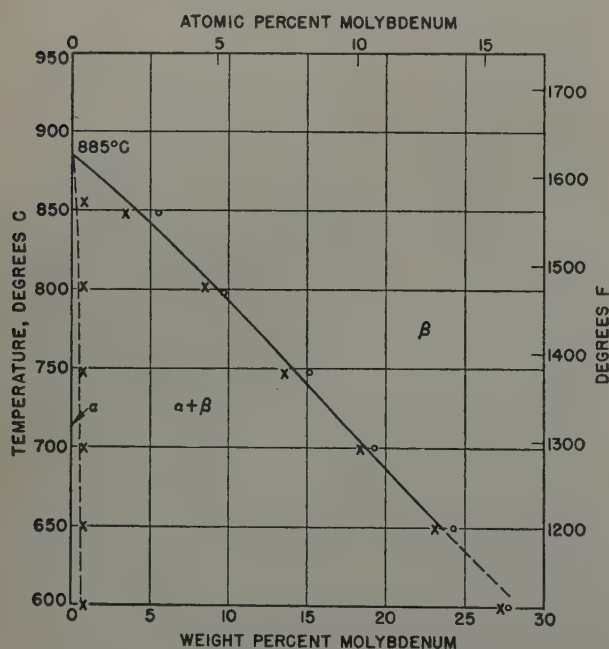
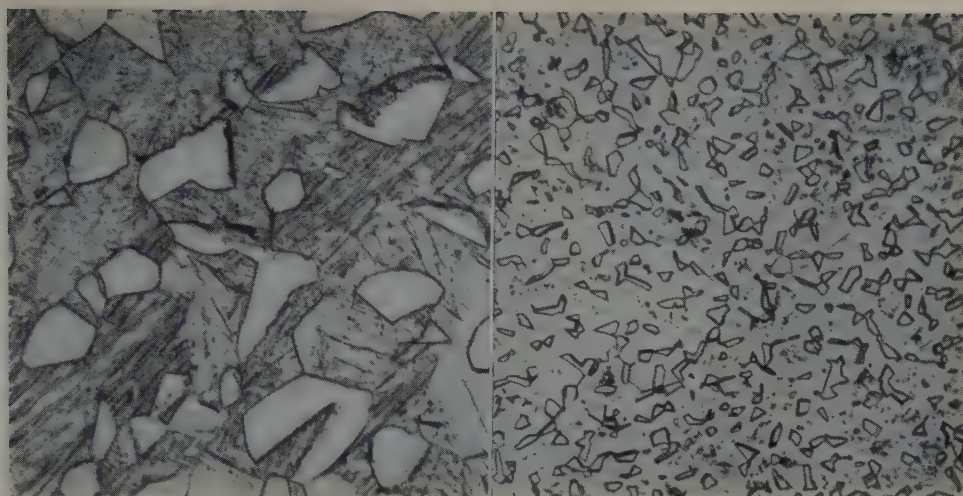


Fig. 3—Extent of the  $\alpha + \beta$  field in iodide titanium-molybdenum alloys.



Fig. 4 (left)—A 2 pct nominal Mo alloy quenched after annealing at 855°C. Isothermally formed  $\alpha$  grains in a matrix of acicular  $\alpha$  transformed from  $\beta$  during the quench. Etchant: 1 pct HF, 3 pct HNO<sub>3</sub> in water. X500.

Fig. 5 (right)—A 2 pct nominal Mo alloy quenched after annealing at 746°C. The predominant phase is retained  $\beta$  and the minor phase is isothermally formed  $\alpha$ . Etchant: 1 pct HF, 3 pct HNO<sub>3</sub> in water. X500.



necessary to homogenize these alloys at high temperatures to promote sufficient diffusion to eliminate the composition gradients.

As Vycor bulbs were found to be unsatisfactory at temperatures greater than 1150°C, a new method was devised for making these high temperature treatments. The specimens were placed in a hole drilled in a titanium ingot and a titanium cap was welded over the top in the arc furnace under conditions similar to those used for melting alloys. By this method, the specimens were enclosed in a gas-tight container which gettered any oxygen or nitrogen present in the furnace atmosphere. Titanium turnings were placed with the specimens to aid in gettering the small amounts of contaminants present in the inert gas used in the arc melting furnace.

The alloys included in the metallographic studies were homogenized for 20 to 40 hr at 1250°C. The beneficial effect of this treatment in removing coring can be seen by comparing the structures of a 50 pct Mo-Process A titanium alloy with (Fig. 1) and without (Fig. 2) previous homogenization treatments.

In spite of the precautions taken to achieve complete homogenization of the higher Cb and Mo-bearing alloys, it was found that some residual coring still persisted in certain of these. While this is not of great importance in interpretation of microstructures of the alloys whose composition clearly places

them in the single-phase  $\beta$  solid solution field, it would tend to affect the placement of the  $\beta/\alpha + \beta$  boundary, especially at the lower temperature levels, where the rate of diffusion is low. A further discussion of this matter will be given in the sections dealing with Ti-Cb and Ti-Mo systems.

**Solidus Determinations:** A high temperature, vacuum induction furnace similar to the one described by Schramm, Gordon and Kaufmann<sup>5</sup> was constructed for determination of solidus temperatures. A description of this unit, details of operation and temperature calibration are available.<sup>4</sup>

Solidus curves and melting points of the metals were established with the aid of this equipment. The technique employed was to heat an alloy of given composition until visual signs of melting were observed, then quench a series of specimens of the same composition at approximately 20°C intervals below the temperature of observed melting, and examine them metallographically for evidence of incipient melting. The estimated accuracy is discussed along with results of the work in succeeding sections of the paper, under systems to which they apply.

**X-ray Diffraction Method:** X-ray diffraction patterns of iodide titanium alloys which retained the  $\beta$  phase at room temperature were taken with a Debye camera and CuK $\alpha$  radiation. The camera radius was 7.18 cm. The exposure conditions were

Table I. Analyses of Metals Used

| Metal                  | Purity,<br>Pct  | Form                                     | Impurities, Pct |    |    |              |             |              |       |             |
|------------------------|-----------------|------------------------------------------|-----------------|----|----|--------------|-------------|--------------|-------|-------------|
|                        |                 |                                          | Fe              | Al | Mn | C            | Co + Ni     | O            | H     | N           |
| Process A<br>Titanium* | 99.71—<br>99.77 | Sponge                                   | 0.10            |    |    | 0.02         |             | 0.140        | 0.006 | 0.005-0.009 |
| Iodide<br>Titanium*    | 99.9+           | Hairpin<br>Bar                           | ✓               | ✓  | ✓  |              |             | ✓            |       | ✓           |
| Columbium              | 99.8+           | 80 mesh<br>powder                        | 0.005           |    |    | 0.074        | Trace       |              |       |             |
| Molybdenum             | 99.9+           | 80 mesh<br>powder;<br>0.003 in.<br>sheet |                 |    |    | 0.015<br>Max | 0.02<br>Max | 0.045<br>Max |       |             |

| Metal                  | Impurities, Pct                |                  |                  |      |    | Hardness<br>Vickers‡ | Source                         |
|------------------------|--------------------------------|------------------|------------------|------|----|----------------------|--------------------------------|
|                        | Ta <sub>2</sub> O <sub>5</sub> | TiO <sub>2</sub> | SiO <sub>2</sub> | Mg   | Si |                      |                                |
| Process A<br>Titanium* |                                |                  |                  | 0.04 |    | 144-159              | E. I. du Pont de Nemours & Co. |
| Iodide<br>Titanium*    |                                |                  |                  | ✓    | ✓  | 74-86                | New Jersey Zinc Co.            |
| Columbium              | 0.10                           | 0.002            | 0.025            |      |    |                      | Fansteel Metallurgical Corp.   |
| Molybdenum             |                                |                  |                  |      |    |                      | Fansteel Metallurgical Corp.   |

\* Supplied by the Air Materiel Command for this work.

† Average spectrographic results of several bars—checks indicate impurities present in 0.05 to 0.001 pct range.

‡ Diamond Pyramid hardness (30 kg load) run on melted buttons.

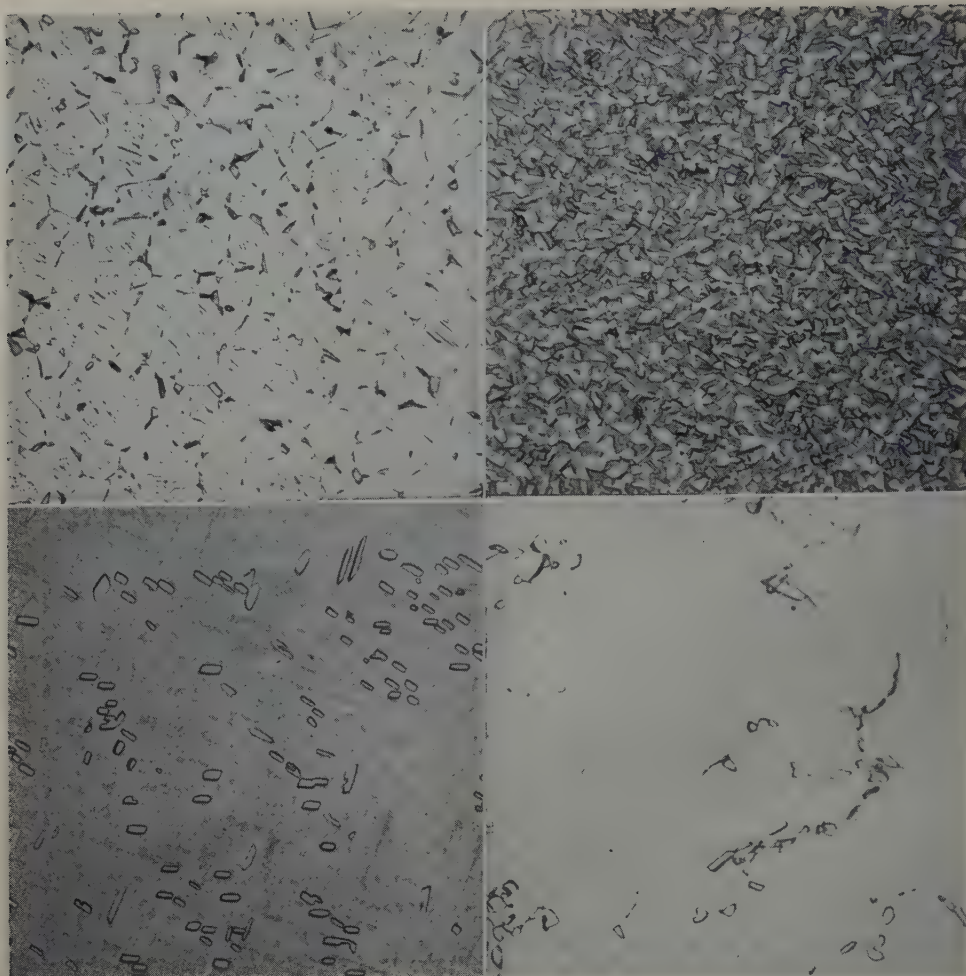


Fig. 6 (upper left)—A 0.75 pct Mo alloy quenched after annealing at 802°C.

Primarily isothermal  $\alpha$  with small particles of  $\beta$  phase included. This alloy is very close to the  $\alpha/\alpha+\beta$  boundary. Etchant: 1 pct HF, 3 pct  $\text{HNO}_3$  in water. X250.

Fig. 7 (upper right)—A 3.4 pct Mo alloy quenched after annealing at 802°C.

A mixture of  $\alpha$  (white) and  $\beta$  (gray - transformed) phases. Etchant: 1 pct HF, 3 pct  $\text{HNO}_3$  in water. X250.

Fig. 8 (lower left)—An 8.4 pct Mo alloy quenched after annealing at 802°C.

Approaching the  $\beta/\alpha+\beta$  boundary. Small  $\alpha$  particles in a matrix of acicular  $\alpha$  transformed from  $\beta$  during the quench. Etchant: 1 pct HF, 3 pct  $\text{HNO}_3$  in water. X250.

Fig. 9 (lower right)—A 9.6 pct Mo alloy quenched after annealing at 797°C.

This alloy is still in the two-phase field, but the  $\beta$  is now retained. Etchant: 1 pct HF, 3 pct  $\text{HNO}_3$  in water. X250.

4 hr at 40 kv and 8 ma, and each line was measured twice. The  $a_s$  values were obtained for each film by extrapolating the plots of  $a$  vs.  $\cos^2\theta$  to  $\cos^2\theta = 0$ .

The alloy specimens were first homogenized for 4 hr at 1400°C and 40 hr at 1250°C. The powders for the X-ray work were then obtained by filing the homogenized samples. The powders were annealed for 1 hr at 860°C in titanium capsules fitted with titanium plugs, and the capsules were sealed in evacuated Vycor bulbs at less than 5 microns pressure. Cooling was effected by quenching the bulbs in cold water. The bulbs were not broken open until

the contents had cooled to room temperature. The powders were then mounted in pyrex capillaries for ease of handling.

### Titanium-Molybdenum System

A limited amount of information exists in the literature on the system Ti-Mo. Kroll<sup>6</sup> has stated that alloys containing up to 5 pct Mo form solid solutions and melt above the melting point of titanium. The Climax Molybdenum Co.,<sup>7</sup> studying Mo-base alloys, found that the solid solubility of titanium in molybdenum is at least 18 to 20 pct. This conclusion was premised upon the identification of second-phase particles as oxides rather than a Ti-Mo intermediate phase. Gonser has stated<sup>8</sup> that, on the basis of powder metallurgical studies,<sup>9</sup> molybdenum has complete solubility in  $\beta$  titanium.

Table II. Analyses of Iodide Titanium-Molybdenum Alloys

| Alloy Designation | Mo, Wt Pct | W, Wt Pct |
|-------------------|------------|-----------|
| IM 0.5-640        | 0.75       | <0.05     |
| IM 1-654          | 1.2        | 0.15      |
| IM 3-653          | 3.4        | 0.20      |
| IM 4-670          | 7.7        | 0.12      |
| IM 5-671          | 5.5        | 0.10      |
| IM 7-673          | 6.5        |           |
| IM 8-674          | 8.4        |           |
| IM 9-675          | 9.6        | 0.07      |
| IM 10-676         | 10.4       |           |
| IM 11-677         | 11.3       |           |
| IM 13-726         | 13.6       |           |
| IM 14-727         | 15.1       |           |
| IM 18-731         | 18.4       |           |
| IM 19-732         | 19.3       |           |
| IM 20-733         | 20.3       | 0.08      |
| IM 23-737         | 23.2       |           |
| IM 24-738         | 24.3       |           |
| IM 27-769         | 27.2       |           |
| IM 28-770         | 27.7       |           |



Fig. 10—A 70 pct nominal Mo alloy homogenized at 1250°C.  $\beta$  solid solution. Etchant: 1 pct HF, 3 pct  $\text{HNO}_3$  in water. X250.



The microstructures of alloys with 1.86, 2.36, 3.82, and 4.65 pct Mo have been examined by Craighead, Simmons and Eastwood<sup>10</sup> after annealing for 30 min at temperatures of 788°, 843°, 871°, 899°, 927°, and 955°C, followed by quenching. According to these data, the maximum solid solubility of molybdenum in  $\alpha$  titanium is less than 1.86 pct within the temperature range studied, and the minimum molybdenum solubility in  $\beta$  titanium is between 3.82 and 4.65 pct at 843°C.

**Results:** The analyses of iodide titanium-molybdenum alloys used in determining the phase diagram are listed in Table II. Although Process A Ti-base alloys were first used to establish the approximate phase boundaries of the system, only the more accurate diagram determined with iodide titanium-base alloys is detailed here.

The  $\alpha + \beta$  field is outlined in Fig. 3. The maximum solubility of molybdenum in  $\alpha$  titanium is about 0.8 pct, and the minimum solubility in  $\beta$  titanium, approximately 28 pct at 600°C. The pretreatment and annealing data for Fig. 3 are summarized in Table III. Figs. 4 and 5 show a 2 pct nominal Mo alloy as treated according to the schedule of Table III and quenched from the temperatures 855° and 746°C, respectively. The decrease in amount of  $\beta$  phase with decreasing temperature

Table III. Schedule of Treatments for Iodide-Titanium-Molybdenum Alloys

| Annealing Temperature, °C | Pretreatment*              | Annealing Time, Hr | Alloys, Pct Mo |
|---------------------------|----------------------------|--------------------|----------------|
| 855                       | P30-36; XR65-78            | 120                | 0.5-2,7,8      |
| 849                       | P8-50; XR64-76             | 90                 | 3-6            |
| 802                       | P8-50; XR63-78             | 160                | 0.5-8          |
| 797                       | P17-44; XR74-80            | 170                | 9-12           |
| 746                       | P11-44; XR65-82            | 200                | 0.5-2,12-19    |
| 700                       | P18-39; XR65-77            | 300                | 0.5-2,18-24    |
| 649                       | P15-39; XR65-77; H, W20-54 | 415                | 0.5-2,20-29    |
| 600                       | P13-38; XR27-76; H, W20-47 | 648                | 0.25-3,24-33   |

\* P—Cold compressed, pct. XR—Cold rolled after compression, pct. H—Homogenized, 1250° or 1400°C. W—Cold rolled, pct.

may be noted. The change in grain size with annealing temperature is also obvious in these figures.

Figs. 6 to 9 are a series of micrographs of alloys containing 0.75, 3.4, 8.4, and 9.6 pct Mo as quenched from approximately 800°C after the treatments scheduled in Table III. This series shows the structures obtained in the traverse across the  $\alpha + \beta$  field. It may be noted that, at this quenching temperature, the  $\beta$  phase has transformed in the 8.4 pct Mo alloy, but is retained in the 9.6 pct alloy.

The  $\beta/\alpha + \beta$  boundary was difficult to establish at the lower temperatures (650° and 600°C), in part due to a slight residual coring despite homogenizing treatments, and partly due to a slow approach to equilibrium during isothermal annealing in this temperature range. The lower end of this curve is therefore shown as a broken line.

The apparent absence of intermediate phases in this system is indicated by the typical structure of a homogenized 70 pct Mo alloy, Fig. 10, which shows a single-phase,  $\beta$  solid solution. The evidence obtained does not entirely exclude the possibility of the existence of a transformation in the Mo-rich alloys at the lower temperature levels. No system-

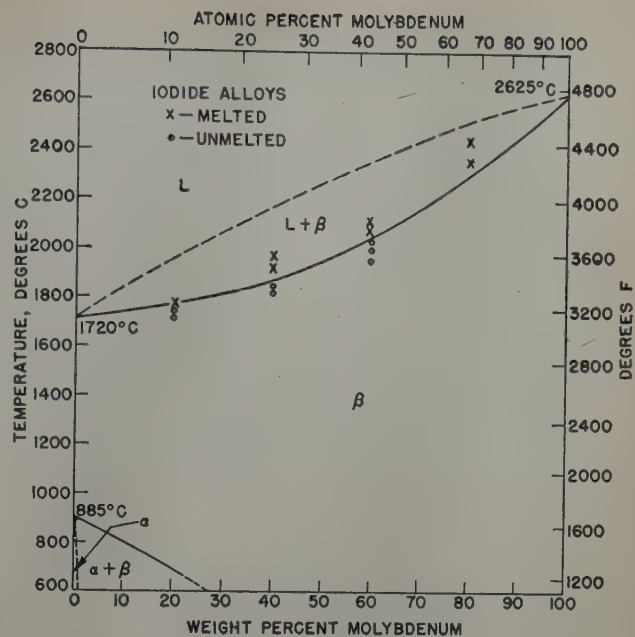


Fig. 11—Iodide titanium-molybdenum phase diagram.

atic search was made in this composition-temperature area.

The overall diagram, including the solidus line, is shown in Fig. 11. The accuracy of this solidus curve is, in general, about  $\pm 25^\circ\text{C}$ . This is determined principally by the quenching increments chosen, which were larger than the precision of temperature measurement in this temperature range. The liquidus curve was drawn in to complete the appearance of the diagram and is not based on experimental data.

**Lattice Parameter Measurements of  $\beta$  Phase of Iodide Titanium-Molybdenum Alloys:** Lattice parameter measurements were made on alloys containing 20, 30, 50, 60, 70, 80, and 90 nominal pct Mo by weight. Body-centered cubic  $\beta$  titanium is isomorphous with molybdenum, and  $\beta$  solid solution may be retained by quenching alloys containing as little as 10 pct Mo from 860°C. All of the alloys used for this work were treated in this manner and revealed single-phase structures microscopically.

The data are plotted vs. composition (atomic percent) in Fig. 12. The molybdenum lattice parameter was taken from Barrett.<sup>11</sup> The lattice para-

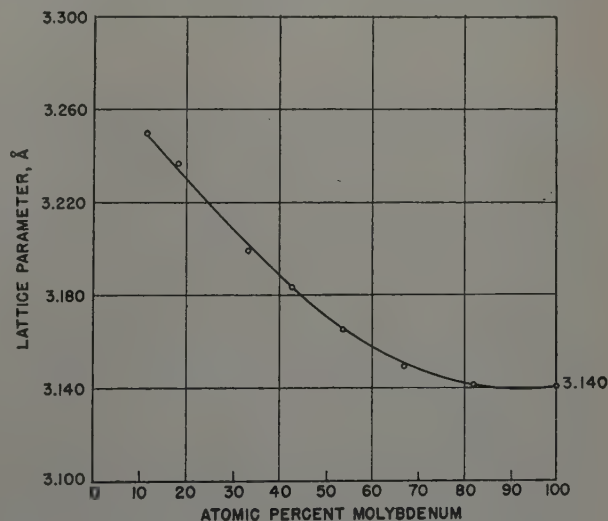


Fig. 12—Lattice parameter-composition curve for Ti-Mo alloys.

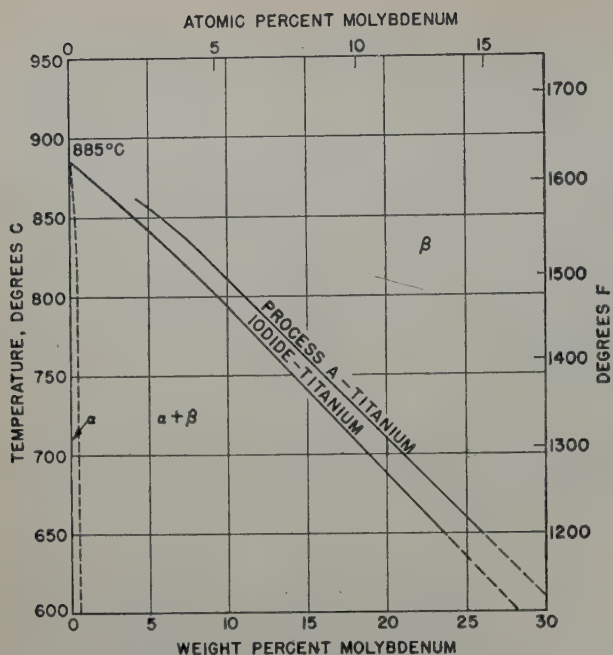


Fig. 13—Comparison of the extent of the  $\alpha+\beta$  fields in the Process A and iodide titanium-molybdenum systems.

meter-composition curves for the Ti-Mo and Ti-Cb systems are based on nominal compositions and therefore can be considered only as qualitative information corroborating the extent of the  $\beta$  solid solution range, rather than quantitative data.

Additions of iodide titanium increase the lattice parameter of molybdenum, but not as a linear function of composition. The parameter curve shows an appreciable negative deviation from Vegard's law.

The Climax Molybdenum Co.<sup>7</sup> has studied the effect of "commercially pure" titanium sponge additions up to about 16 pct (weight) on the lattice parameter of molybdenum. Although the Climax work cannot be compared very readily with the present findings because of the differences in titanium used, type of X-ray specimen, and treatment of specimens, the trend of the parameter curve (indicating strong deviation from Vegard's law) is in general agreement with that of the present data.

The 60, 70, 80, and 90 wt pct Mo alloys displayed diffraction patterns containing low angle lines foreign to the body-centered cubic structures. Solid specimens, treated in a manner identical to that for the X-ray powders, failed to reveal a new phase microscopically. The source of these extra lines was not discovered.

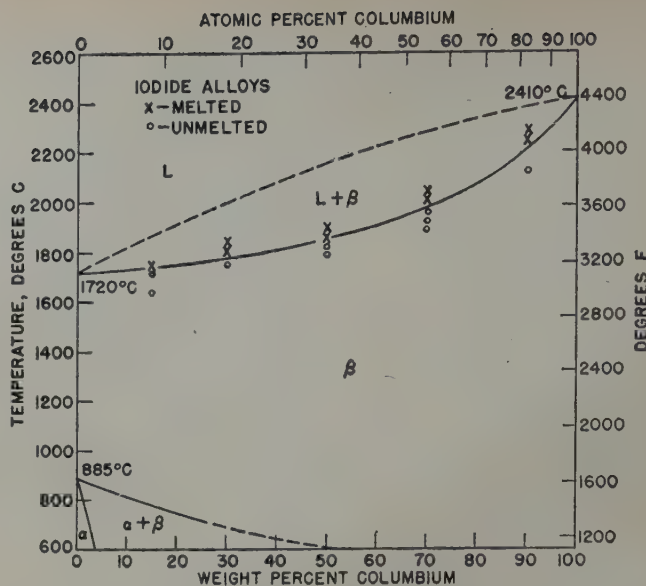


Fig. 16—Iodide titanium-columbium phase diagram.

**Comparison of the Ti-Mo Diagrams:** A comparison between the solid state phase diagrams of iodide titanium-molybdenum and Process A Ti-Mo alloys is depicted in Fig. 13. The  $\beta/\alpha + \beta$  curve for Process A alloys was not extended to 100 pct Ti because it is well known that the transformation of Mg-reduced titanium occurs over a range of temperature. The entire  $\alpha + \beta$  field is broadened by the use of Process A metal rather than iodide titanium. This was expected to be the case in view of the known effect of oxygen and nitrogen in raising the transformation temperature and stabilizing the  $\alpha$  phase.<sup>12</sup> The difference is illustrated by Figs. 14 and 15. Fig. 14 shows a 15.1 pct Mo alloy (iodide base) heat treated at 746°C. The structure consists entirely of  $\beta$  solid solution. Fig. 15 is a 15.6 pct Mo alloy (Process A base) quenched from the same temperature after long annealing. This alloy still contains a considerable amount of  $\alpha$  phase.

The solidus curves determined for the two types of alloys superimpose upon one another within the limits of accuracy of the method; therefore no overall diagram comparison of Process A vs. iodide alloys is presented.

### Titanium-Columbium System

No prior investigation of the phase diagram of this system has been reported. However, Gonser<sup>8</sup> has

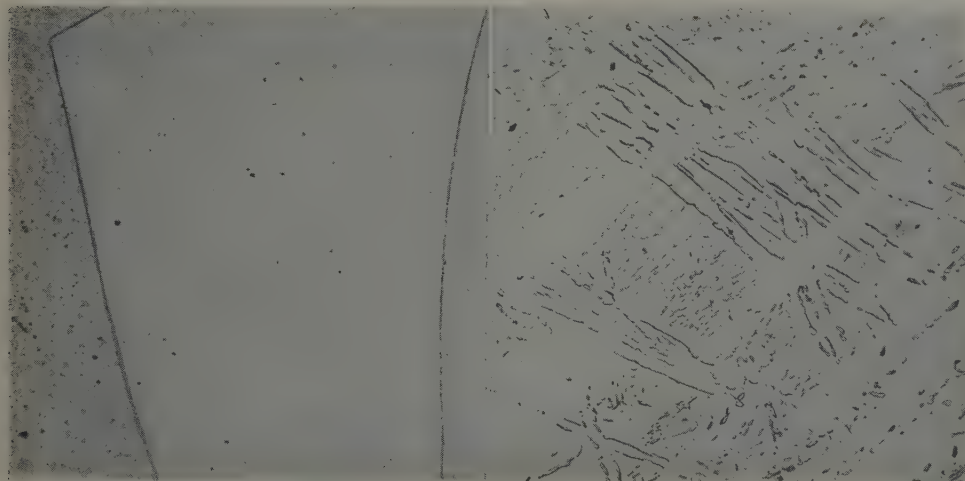


Fig. 14 (left)—A 15.1 pct Mo (iodide titanium) alloy quenched after annealing at 746°C. Single phase  $\beta$  solid solution. Etchant: 1 pct HF, 3 pct HNO<sub>3</sub> in water. X250.

Fig. 15 (right)—A 15.6 pct Mo (Process A titanium) alloy quenched after annealing at 746°C. Two-phase structure:  $\alpha$  platelets in retained  $\beta$  matrix. Comparing this with Fig. 14 shows that the  $\beta/\alpha + \beta$  boundary extends to higher molybdenum content for Process A titanium-base alloys than for iodide titanium-base alloys. Etchant: 1 pct HF, 3 pct HNO<sub>3</sub> in water. X250.



reported that columbium and  $\beta$  titanium form a continuous series of solid solutions. This conclusion is based on results of powder metallurgical studies.<sup>9</sup>

**Results:** The phase boundaries of the  $\alpha$  and  $\beta$  solid solutions were determined by micrographic analysis of iodide titanium-base alloys covering the range 0 to 50 pct Cb in approximately 1 pct steps. Alloys with 40, 50, 60, 70, 80, and 90 pct Cb were used for X-ray diffraction measurement of the  $\beta$  phase lattice parameters, and microscopic examination of samples in a limited number of heat-treated states. Nominal compositions have been used for plotting the results of microscopic observations, because no reliable analytical methods were available for the determination of columbium in titanium alloys. As all iodide-titanium alloy ingots were weighed carefully immediately after melting, and the weight losses were negligible, the nominal compositions were believed acceptable.

Fig. 16 shows the phase diagram of the whole system, and Fig. 17 is an enlarged view of the  $\alpha + \beta$  field. Annealing temperatures lower than 600°C were not used, since it appears that equilibrium would be almost impossible to achieve, even after long-time annealing at these temperature levels. The

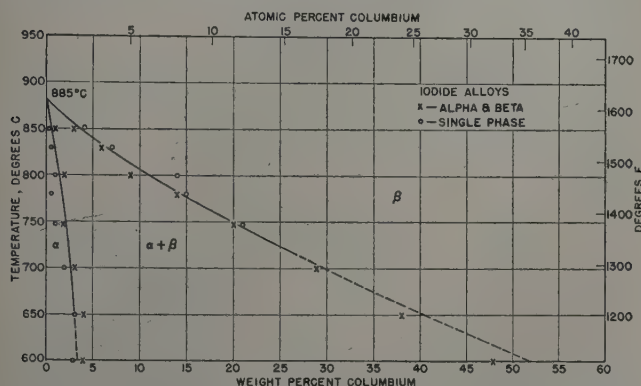


Fig. 17—Extent of the  $\alpha + \beta$  field in the iodide titanium-columbium system.

alloys were annealed at eight temperature levels between 600° and 850°C. Table IV gives the pretreatment and annealing data.

As the micrographs shown in the section on the Ti-Mo system are considered representative of both diagrams, duplicate structures are not presented in this section.

The solubility of columbium in  $\alpha$  titanium was found to increase with lowered temperatures to about 4 pct Cb at 600°C. The  $\beta/\alpha + \beta$  boundary could be determined with certainty above 750°C.

Table IV. Schedule of Treatments for Iodide Titanium-Columbium Alloys

| Annealing Temperature, °C | Pretreatment*      | Annealing Time, Hr | Alloys, Pct Cb |
|---------------------------|--------------------|--------------------|----------------|
| 850                       | P55-60; XR60-85    | 70                 | 1-9            |
| 828                       | P55-60; XR60-85    | 135                | 0.5, 6-9       |
| 802                       | P55-60; XR60-85    | 160                | 1-3, 5-9       |
| 775                       | P45-60; XR55-80    | 230                | 0.5, 14-19     |
| 746                       | P55-60; XR60-85    | 200                | 1-5            |
|                           | P20-45; XR5-75     |                    | 18-28          |
| 700                       | P55-60; XR60-85    | 335                | 2-5            |
|                           | P15-40; XR45-75; H |                    | 29-34          |
| 649                       | P55-60; XR60-85    | 415                | 3-7            |
|                           | P40-50; XR80; H    |                    | 36-44          |
| 600                       | P55-60; XR60-85    | 648                | 0.5-7          |
|                           | P30-45; XR75; H    |                    | 47-50, 60      |

\* P—Cold compressed, pct. XR—Cold rolled after compression, pct. H—Homogenized, 1250° or 1400°C. W—Cold rolled, pct.

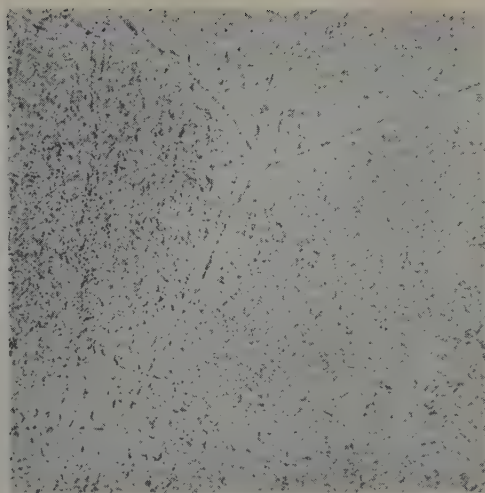


Fig. 18—A 48 pct nominal Cb alloy homogenized, cold pressed, and quenched after annealing at 600°C. Very fine distribution of  $\alpha$  precipitate in retained  $\beta$ . Etchant: 1 pct HF, 3 pct HNO<sub>3</sub> in water. X250.

The phase boundary at 700°C, however, could not be located accurately, because of the presence of some residual coring due to lack of complete homogeneity. For example, alloys containing 29 to 34 pct Cb, even after homogenization for 40 hr at 1250°C, cold working, subsequent annealing at 700°C, and quenching, showed very small amounts of  $\alpha$  phase (estimated to be within 1 to 3 pct) in a matrix of transformed  $\beta$ . The transformation of  $\beta$  to acicular  $\alpha$  occurred in all alloys containing less than 36 pct Cb. With higher columbium contents, the  $\beta$  phase was retained on quenching.

The alloys quenched from 650° and 600°C were also subjected to homogenization for 40 hr at 1250°C prior to the final long-time anneal. Even so, all alloys selected for bracketing the phase boundary at 650°C (36 to 44 pct Cb) and 600°C (47 to 60 pct Cb) contained small amounts of the  $\alpha$  phase, varying somewhat irregularly in amount with composition, see Fig. 18. For this reason, the  $\beta/\alpha + \beta$  boundary of Fig. 17 is dotted for temperatures at and below 700°C. This extrapolation of the solid curve is believed to represent conditions close to equilibrium.

In order to determine the constitution of the Cb-rich alloys, specimens with 50, 60, 70, 80, and 90 pct Cb were homogenization-annealed for 4 hr at 1400°C and 40 hr at 1250°C. Fig. 10 is representative of the structures of these alloys, indicating that the  $\beta$  field extends over the entire composition range at high temperatures.

As a further check, the lattice parameters of the  $\beta$  phase between 40 and 90 pct Cb (25.8 and 83.1 atomic pct) were determined. The data are plotted in Fig. 19. Additions of iodide titanium decrease the lattice parameter of columbium. This change follows a small negative deviation from Vegard's law.

As was the case with Ti-Mo alloys, the diffraction

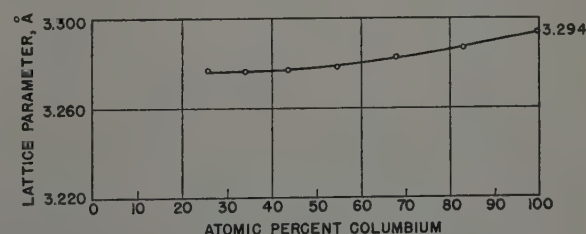


Fig. 19—Lattice parameter-composition curve for Ti-Cb alloys.

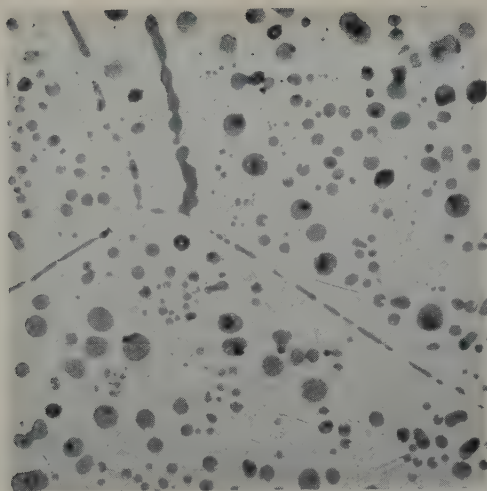


Fig. 20—A 90 pct nominal Cb alloy homogenized then heated to a temperature above the solidus curve, 2245°C, and quenched. The "bubbles" in the structure are typical signs of incipient melting. Etchant: 1 pct HF, 3 pct HNO<sub>3</sub> in water. X250.

patterns of alloys with 70, 80, and 90 pct Cb contained lines foreign to the body-centered cubic solid solution in low angle regions of the film, which were not successfully identified. Solid specimens, heat treated in the same manner as the X-ray powders, did not reveal microscopic evidence of a transformation in this composition range. This single treatment, however, does not completely rule out the possibility of a low temperature transformation in this system.

The solidus curve shown in Fig. 16 was determined with homogenized alloys. The microscopic evidence of incipient melting for all of these alloys is exemplified by Fig. 20, showing a 90 pct Cb alloy quenched from above the solidus temperature. The overall accuracy of this curve is limited by the temperature increments employed in the incipient fusion method. For this diagram, the accuracy may be taken as  $\pm 25^\circ\text{C}$ .

The solidus temperature increases continuously with increasing columbium content. The melting point of iodide titanium was found to be  $1720^\circ\text{C}$ , as compared with  $1727^\circ\text{C}$  given by deBoer.<sup>13</sup> The melting point of columbium is reported as  $2415 \pm 15^\circ\text{C}$ ;<sup>14</sup> it was determined experimentally to be  $2410^\circ\text{C}$ . The dotted liquidus curve in Fig. 16 was not determined experimentally but was included to complete the appearance of the diagram.

The features of the Process A titanium-columbium phase diagram are similar to those of the iodide titanium-columbium phase diagram. The difference appears to be that the  $\alpha + \beta$  field in the Process A titanium alloys is somewhat wider than that in the iodide titanium alloys. This same relationship was found for the Ti-Mo alloys described in the previous section.

### Summary

**Titanium-Molybdenum:** Ti-Mo phase diagrams were determined with both DuPont Process A and iodide titanium-base alloys. Both diagrams have the following features:  $\beta$  titanium and molybdenum form a continuous series of solid solutions. A constantly rising solidus curve connects the melting points of titanium and molybdenum. The  $\alpha$  to  $\beta$  transformation temperature of titanium ( $885^\circ\text{C}$ ) is lowered by the addition of molybdenum, with a broadening of the  $\alpha + \beta$  field with decreasing temperature.

The solubility of molybdenum in  $\alpha$  titanium is less than 0.8 pct Mo at temperatures between  $885^\circ$  and

$600^\circ\text{C}$  for both Process A and iodide titanium-base alloys. The  $\beta/\alpha + \beta$  boundary is essentially a straight line in both phase diagrams. For iodide-base alloys, it extends from the transformation temperature of titanium to about 24 pct Mo at  $650^\circ\text{C}$ . Impurities in Process A titanium shift the  $\beta/\alpha + \beta$  boundary at  $650^\circ\text{C}$  to about 26 pct Mo. X-ray diffraction results show that molybdenum additions decrease the lattice parameter of  $\beta$  titanium in accordance with a negative deviation from Vegard's law.

**Titanium-Columbium:** The Ti-Cb phase diagram determined with iodide titanium-base alloys has the following features:  $\beta$  titanium and columbium form a continuous series of solid solutions, and the solidus curve constantly rises from the melting point of titanium to that of columbium. Columbium lowers the  $\alpha$  to  $\beta$  transformation temperature of titanium, with the resulting  $\alpha + \beta$  field broadening with decreasing temperature. The solubility of columbium in  $\alpha$  titanium increases with fall in temperature to about 3 pct Cb at  $600^\circ\text{C}$ . The  $\beta/\alpha + \beta$  boundary for  $850^\circ$ ,  $800^\circ$ , and  $750^\circ\text{C}$  lies at 3.5, 10.5, and 20 pct Cb, respectively. Because some residual coring remained in the heat treated alloys with more than 25 pct Cb, even after homogenization annealing treatments, this curve could not be determined with high accuracy for temperatures of  $700^\circ\text{C}$  and lower. However, there is certain evidence to indicate that it lies close to 30 pct Cb at  $700^\circ\text{C}$ , and between 50 and 55 pct Cb at  $600^\circ\text{C}$ . X-ray diffraction results show that columbium additions increase the lattice parameter of  $\beta$  titanium in accordance with a small negative deviation from Vegard's law.

### Acknowledgments

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# On the Mechanism and Kinetics of the Scaling of Iron

by M. H. Davies, M. T. Simnad, and C. E. Birchenall

The transport mechanisms previously proposed in wüstite and hematite have been confirmed by movement of inert markers during the growth of these phases. By similar measurements the mechanism for magnetite has been determined. The rates of growth of multilayer scales on iron, magnetite and hematite on wüstite, and hematite on magnetite have been measured. All rates are found to be diffusion controlled under the conditions of the experiments.

MANY studies have been made of the rate of oxidation of iron in both the low temperature, film-forming region and the high temperature scaling range. The interpretation of the results has been greatly complicated by the formation of multilayered scales containing the various phases of iron oxides. In most cases no attempt has been made to determine the composition of the scale and its dependence on time of oxidation in a quantitative manner. However, several recent studies<sup>1-3</sup> have taken this variable into account.

It is generally agreed that the growth of thick scales on iron follows a parabolic rate law for the increase of total thickness. In the thin film region agreement has been claimed with parabolic equations of various forms and with logarithmic equations. The discussion here will be concerned only with the formation of scales of considerable thickness, greater than several microns, although some of the conclusions may be applicable to thin films.

A brief survey will be given of the solid phases of the iron-oxygen system, the stability of wüstite in bulk and in thin films, the relative densities of iron in the metal and oxides, and the kinetics of forma-

tion of oxide scales on iron. New experimental results will be introduced at several points during the discussion, and an attempt will be made to formulate a mechanistic picture consistent with these observations. The experimental techniques are described in an appendix.

## Iron-Oxygen System

Fig. 1a shows the iron-oxygen phase diagram.

**Wüstite ("FeO"):** The lowest of the oxides has a NaCl type cubic lattice formed by close-packing of the relatively large oxide ions with the smaller iron ions arranged in the interstices. The ionic radius for  $O^{2-}$  is about 1.3 Å, while  $Fe^{2+}$  has a radius of about 0.8 Å and  $Fe^{3+}$  about 0.7 Å. Its range of existence on the phase diagram is very wide for an ionic material of this type and does not seem to include the stoichiometric composition FeO. These deviations appear to be well established as vacancies on iron lattice sites by the comparison of lattice parameters and densities for a series of compositions by Jette and Foote.<sup>4</sup> The limits of the field are disputed, but the work which seems most reliable<sup>5</sup> indicates vacancies in from 5 pct to more than 12 pct of the iron sites. In order for the crystal to be electrically neutral, there must be electron holes which correspond to the formation of trivalent iron ions equal to twice the number of vacancies.

**Magnetite ("Fe<sub>3</sub>O<sub>4</sub>"):** Considerable disagreement also exists in the literature about the stable range of the Fe<sub>3</sub>O<sub>4</sub> field. Some diagrams show the Fe<sub>3</sub>O<sub>4</sub> composition to be lower in oxygen than the formula indicates, but Schenck<sup>6</sup> gives a diagram from the

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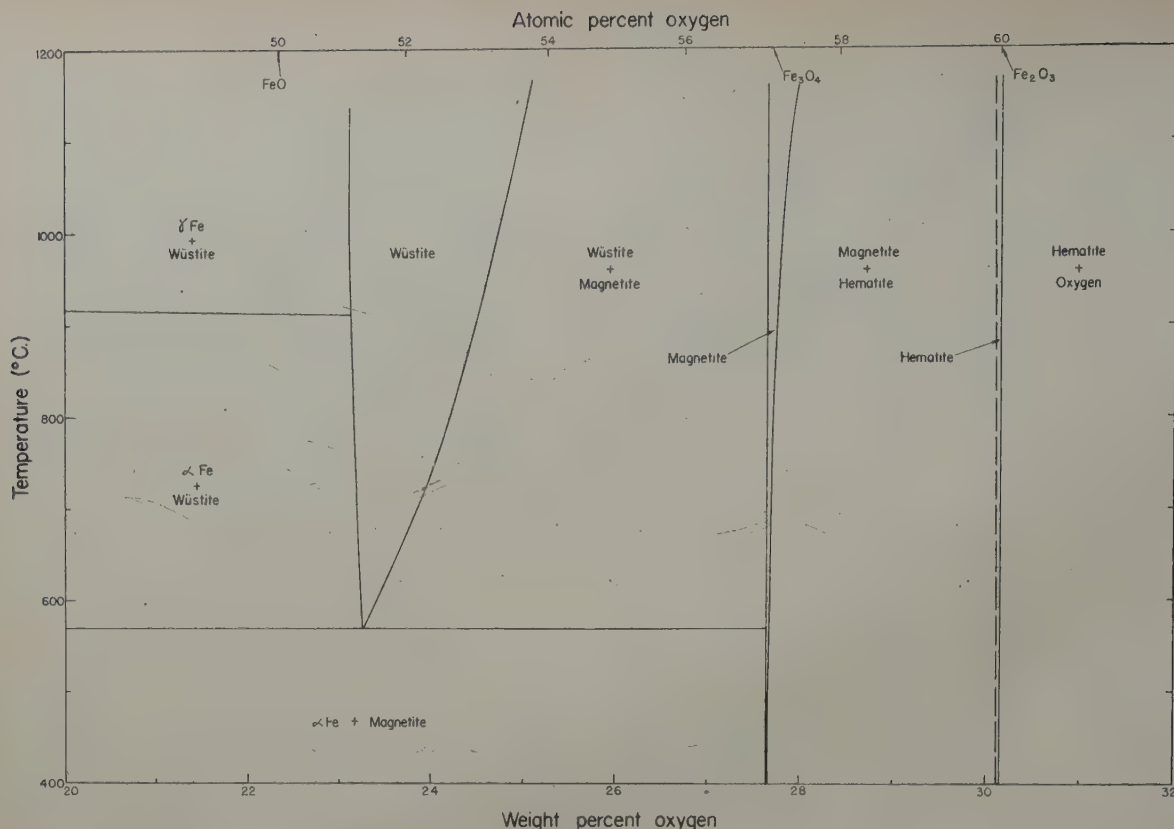


Fig. 1a

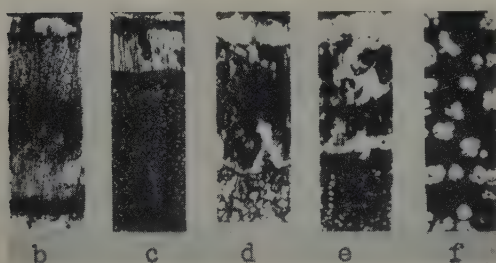


Fig. 1—*a*—Iron-oxygen phase diagram, schematic.

- b*—Iron oxidized at 900°C for 100 min. X150.  
Iron | "FeO" + proeutectoid  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_2\text{O}_3$ .
- c*—Iron oxidized at 975°C for 100 min. X150.  
"FeO" + proeutectoid  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_2\text{O}_3$ .
- d*—Iron oxidized at 850°C for 900 min. X150.  
"FeO" + proeutectoid  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_2\text{O}_3$ .
- e*—Iron oxidized at 1000°C for 900 min. X150.  
"FeO" + proeutectoid  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_3\text{O}_4$  |  $\text{Fe}_2\text{O}_3$ .
- f*—Proeutectoid magnetite in matrix of wüstite. X500.

work of Benedicks and Lofquist<sup>7</sup> which indicates an oxygen excess. Darken and Gurry<sup>8</sup> report similar results. More recent studies by Verwey and Haayman<sup>9</sup> based upon X-ray parameter studies and the measurement of electronic conductivities support the latter. They believe that  $\text{Fe}_3\text{O}_4$  can increase its oxygen content by forming regions closely resembling  $\gamma\text{Fe}_2\text{O}_3$  which has a structure similar to  $\text{Fe}_3\text{O}_4$ . Both of these oxides are cubic with their structures largely determined by the close-packing of oxide ions, so the correspondence is not surprising.

**Hematite ("Fe<sub>2</sub>O<sub>3</sub>"):** The hematite ( $\alpha\text{Fe}_2\text{O}_3$ ) field probably is slightly oxide ion deficient, since the divalent and trivalent states of oxidation are the only ones readily available to iron. This is confirmed by the conductivity studies of Bevan, Shelton, and Anderson,<sup>9</sup> who conclude that the deficiency leads to oxide site vacancies or interstitial iron ions. Ionic transport in this phase is probably by oxide ions as compared with wüstite where iron is almost certainly the mobile constituent. Pryor and Evans<sup>10</sup> make use of this in explaining the dissolution behavior of hematite in acids. Preliminary diffusion measurements for iron in hematite by Himmel<sup>11</sup> indicate a negligible diffusion rate for iron ions, favoring transport by oxide vacancies rather than interstitial iron ions.

In addition to  $\alpha\text{Fe}_2\text{O}_3$ , a cubic form,  $\gamma\text{Fe}_2\text{O}_3$ , may be prepared by dehydration of  $\gamma\text{FeOOH}$  below 500°C or by oxidation of  $\text{Fe}_3\text{O}_4$  up to 400°C. When  $\gamma\text{FeOOH}$  is dehydrated above 500°C,  $\alpha\text{Fe}_2\text{O}_3$  forms. If the dehydration product formed below 500°C is held above 350°C, it will eventually transform to  $\alpha\text{Fe}_2\text{O}_3$ . Above 400°C  $\text{Fe}_3\text{O}_4$  oxidizes to  $\alpha\text{Fe}_2\text{O}_3$ . Although transformation temperatures are given in the range of 150° to 400°C, no evidence could be found in the literature for the transformation of  $\alpha\text{Fe}_2\text{O}_3$  to  $\gamma\text{Fe}_2\text{O}_3$  at any temperature. In fact, Fricke and his co-workers<sup>12</sup> have measured heats of solution of both forms in acid at 20° to 32°C and found that  $\gamma\text{Fe}_2\text{O}_3$  has a heat content in excess of that of  $\alpha\text{Fe}_2\text{O}_3$  of more than 6 kcal per mol for crystals of the same particle size. It appears that  $\gamma\text{Fe}_2\text{O}_3$  is a metastable growth form which is the product of dehydration of  $\gamma\text{FeOOH}$  and of the oxidation of  $\text{Fe}_3\text{O}_4$  because of its resemblance in structure to the reactants.

$\alpha\text{Fe}_2\text{O}_3$ , the only form to be considered here, is a rhombohedral crystal<sup>13</sup> (the  $\alpha$  corundum structure) with the oxide ions in nearly close-packed hexagonal arrangement. The iron ions reside in the interstices.

#### Eutectoid Decomposition of Wüstite

Chaudron and Forestier<sup>14</sup> studied this reaction on bulk "FeO" and found that the process behaved as



a normal nucleation and growth process with a maximum rate at about 470°C, as shown in Fig. 2. They also found the iron metal precipitated at the oxide grain boundaries.

Although the normal transformation temperature is about 570°C, Gulbransen and Hickman<sup>15</sup> have shown that in thin films upon Fe, "FeO" exists at temperatures as low as 400°C. This lower limit of existence is strongly dependent upon film thickness and shifts toward 570°C as the film becomes thicker. When the transformation occurs on cooling, little iron is found in the oxide, so it is possible that, when the film is thin and an iron substrate is present, the iron may diffuse back to the interface and plate out on the substrate.

More recently Gulbransen and Ruka<sup>16</sup> have carried out an electron diffraction investigation of this reaction, the reverse reaction, and also reactions involving  $\alpha\text{Fe}_2\text{O}_3$  in films on metal surfaces. They confirmed the above results and eliminated former discrepancies between phases reported in scales by electron diffraction methods as compared with X-ray and micrographic techniques.

### Relations Between Phases

Bozorth,<sup>17</sup> Pfeil,<sup>18</sup> Heindlhofer and Larsen,<sup>19</sup> and Fischbeck and Salzer<sup>20</sup> have demonstrated that in strongly oxidizing atmospheres and at temperatures somewhat above 570°C the oxides of iron form in successive layers on the metal in accordance with the principle of LeChatelier, the lowest valence oxide next to the metal, the highest in contact with the atmosphere. At room temperature the densities of iron ions in the metal and oxides in the above

order are:  $7.85 \frac{\text{g Fe}}{\text{cc Fe}}$ ,  $4.43 \frac{\text{g Fe}}{\text{cc FeO}}$ ,  $3.74 \frac{\text{g Fe}}{\text{cc Fe}_3\text{O}_4}$ ,  $3.67 \frac{\text{g Fe}}{\text{cc Fe}_2\text{O}_3}$ . It is evident that the system fulfills

the density ratio conditions of Pilling and Bedworth<sup>21</sup> for the formation of continuous layers.

At the interfaces between successive layers definite orientation relationships have been observed. McCandless and Mehl<sup>22</sup> have studied wüstite formed on Fe and found that there is a (001) plane of iron atoms common to both phases, with the 010 direction of wüstite parallel to the 110 direction of Fe. The same investigators concluded that wüstite and magnetite had a common (001) plane of oxide ions. Similarly, between magnetite and hematite Gruner<sup>23</sup> showed the matching in an oxide ion plane of the basal (0001) plane of  $\alpha\text{Fe}_2\text{O}_3$  with the (111) plane of  $\text{Fe}_3\text{O}_4$ . The disorder of iron ion in crossing this last interface is quite large, but in the  $\text{FeO-Fe}_3\text{O}_4$  case the iron positions on either side of the common plane are partially in fair agreement.

No specific study of the relationship between  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{Fe}_2\text{O}_3$  seems to have been made, but the two give practically indistinguishable electron diffraction patterns, so that a match on the cubic oxide ion planes seems likely. More important is the relationship between  $\gamma\text{Fe}$  and wüstite which has not been determined. That coherency exists is indicated from the fact that protective scales form. Only a common iron plane is possible. The results of Fischbeck and Salzer<sup>20</sup> may indicate the fit is sufficiently poor to constitute an appreciable resistance, but nothing in the new work reported here confirms this.

Goldschmidt<sup>24</sup> has examined the relative volumes and structures of the metal and the cubic oxides and

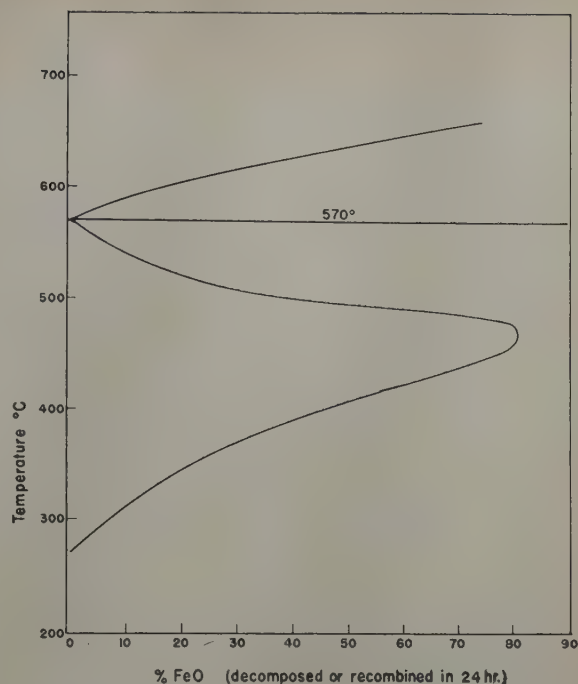


Fig. 2—Decomposition of wüstite (after Chaudron and Forestier) showing percentage of "FeO" decomposed or recombined in 24 hr.

obtained numerical comparisons which illustrate the smallness of the adjustments which must be made to fit the lattices together at an interface.

### Transport Mechanisms

The transport mechanisms in oxides may be studied in at least three different ways.

1—The electrical conductivity<sup>25</sup> may be studied at several temperatures as a function of the partial pressure of oxygen in equilibrium with the specimen.

2—Self-diffusion coefficients<sup>26</sup> of both ions may be determined in the oxide.

3—"Kirkendall effects," the movement of inert markers in the diffusing systems, may be measured as first attempted by Pfeil<sup>18</sup> in 1929. Pfeil used slurries of  $\text{NiO}$  or  $\text{Cr}_2\text{O}_3$  painted on the metal surfaces as inert markers. After oxidizing the surface, he sought the position of the markers in the oxide. The results were not conclusive. The markers were found in the wüstite layer, but the layer was mechanically separated into two parts at the point where the impurities were concentrated. The location of the markers appears to have been determined partly by the mechanical separation of scale from metal during oxidation.

New measurements of this last type have been made using radioactive silver as inert markers. This has many advantages for this particular application since it neither dissolves in the metal and its oxides, nor oxidizes at these temperatures. Furthermore, very small amounts can be detected on a polished cross-section by autoradiographic methods, so that very thin deposits of silver may be used. These were applied by wetting a silk thread in active silver nitrate solution and touching each side of the iron or iron oxide plates twice or more, leaving parallel wet marks. These were dried and the silver nitrate decomposed to silver in the preliminary heating of the sample before oxidation began.

Three series of these studies were carried out: 1—iron metal was marked, then scaled in oxygen to give a multilayer scale; 2—wüstite was marked, then reacted completely to magnetite in water vapor;

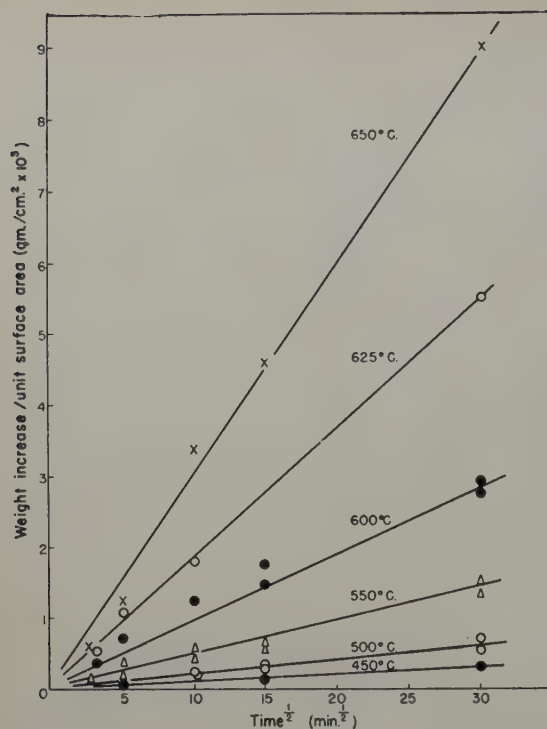


Fig. 3a—Isothermal curves for the rate of increase of weight of iron oxidized in oxygen.

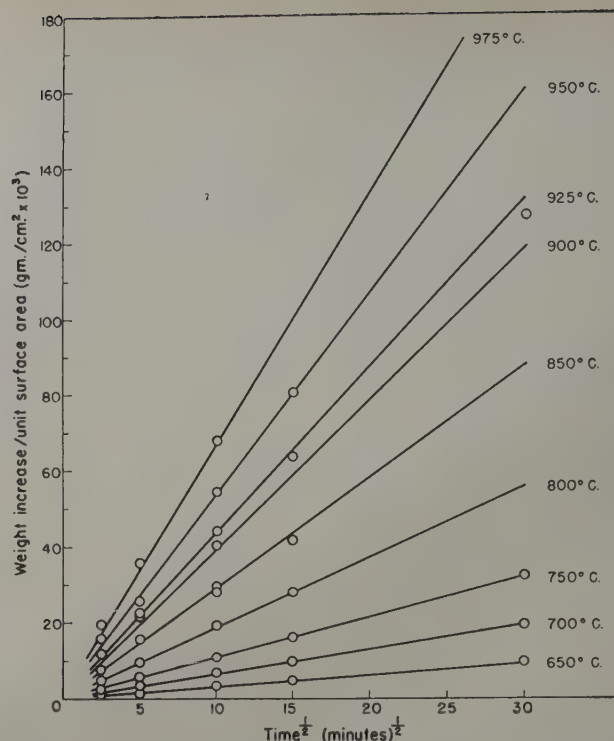


Fig. 3b—Isothermal curves for the rate of increase of weight of iron oxidized in oxygen.

3—magnetite was marked, then partially reacted to hematite in oxygen. In case 1 the markers were found precisely at the metal-oxide interface. In case 2 the markers were found almost at the outside surface. In case 3 the markers could not be found. It was concluded that the silver remained on the outer surface, from which it vaporized during the long oxidation treatment required to form an appreciably thick layer of the slowly growing hematite.

From these measurements the following conclusions may be drawn about the transport mechanisms leading to the growth of the oxides of iron:

1—Wüstite grows almost entirely by diffusion of iron ions. Oxide ions are added at the outer face of the phase and remain essentially fixed.

2—Magnetite grows largely by oxide ion diffusion (which may indicate a need for review of the deviations of the phase field from the stoichiometric  $\text{Fe}_3\text{O}_4$  composition), but there seems to be an appreciable contribution from iron ion diffusion—about 20 pct.

3—Hematite grows by oxide ion diffusion with practically no iron ion participation. Iron ions are added at the inner face and stay fixed.

These findings are in accord with the information available on wüstite and hematite, the former cation conducting, the latter anion conducting. The new result on magnetite is rather surprising, but not in conflict with any previous work known to the

authors. This is being checked by method 2 in this laboratory.

#### Kinetics of Oxidation

In the many studies of the oxidation of iron to form multilayered scales, fairly good agreement for the rate constants over most of the temperature range investigated has been obtained. However, at the higher temperatures discontinuities have been reported in the plot of the variation of the logarithm of  $k$ , the parabolic rate constant, against the reciprocal of the absolute temperature. This discontinuity has been attributed both to the effect of the magnetic transformation in iron at  $760^\circ\text{C}$  and also to the  $\alpha$  to  $\gamma$  phase transformation at  $910^\circ\text{C}$ .<sup>1,20</sup> In the endeavor to resolve this controversy and also to check the work of Benard and Coquelle<sup>1</sup> on the kinetics of growth of the individual phases in the scale, it was decided to investigate the oxidation of iron over the temperature range  $400^\circ$  to  $1200^\circ\text{C}$  under very precisely controlled conditions.

A full account of the experimental methods and techniques is given in the appendix, but it is well to point out the essential differences here. With the exception of Gulbransen and others in work on the kinetics of formation of thin films, 1—oxidation studies have generally employed air, subject to variation in composition and humidity as the oxidizing medium; 2—oxidation has been allowed to proceed

Table I. Approximate Values for the Relative Percentages of "FeO",  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}_2\text{O}_3$  in Scales Formed on Iron Oxidized in Oxygen

| Temperature, $^\circ\text{C}$ | Time, Min | "FeO," Pct | $\text{Fe}_3\text{O}_4$ , Pct | $\text{Fe}_2\text{O}_3$ , Pct | Time, Min | "FeO," Pct | $\text{Fe}_3\text{O}_4$ , Pct | $\text{Fe}_2\text{O}_3$ , Pct | Time, Min | "FeO," Pct | $\text{Fe}_3\text{O}_4$ , Pct | $\text{Fe}_2\text{O}_3$ , Pct |
|-------------------------------|-----------|------------|-------------------------------|-------------------------------|-----------|------------|-------------------------------|-------------------------------|-----------|------------|-------------------------------|-------------------------------|
| 600                           | 100       | 50         | 50                            |                               | 225       | 50         | 50                            |                               | 900       | 55         | 45                            |                               |
| 625                           | 110       | 70         | 30                            |                               | 225       | 75         | 25                            |                               |           |            |                               |                               |
| 700                           | 225       | 98         | 2                             |                               | 900       | 97         | 3                             |                               |           |            |                               |                               |
| 750                           | 100       | 96         | 4                             |                               | 900       | 94         | 6                             |                               |           |            |                               |                               |
| 800                           | 100       | 96         | 2                             | 2                             | 225       | 92         | 4                             | 4                             | 900       | 98         | 2                             | <1                            |
| 850                           | 225       | 96         | 4                             | <1                            | 900       | 96         | 3                             | <1                            |           |            |                               |                               |
| 900                           | 100       | 90         | 9                             | <1                            | 225       | 90         | 9                             | <1                            | 900       | 92         | 7                             | <1                            |
| 975                           | 100       | 96         | 3                             | <1                            | 225       | 96         | 3                             | <1                            | 900       | 95         | 4                             | <1                            |
| 1000                          | 25        | 95         | 1                             | <1                            | 225       | 96         | 2                             | <1                            |           |            |                               |                               |
| 1035                          | 49        | 95         | 4                             | <1                            | 64        | 95         | 4                             | <1                            |           |            |                               |                               |
| 1090                          | 25        | 94         | 5                             | <1                            | 49        | 94         | 5                             | <1                            |           |            |                               |                               |



during the initial heating period before the specimen reaches the temperature of the furnace. In the present series of experiments pure dry oxygen was used and in addition the time and surface for the beginning of oxidation were precisely defined. This was accomplished by first heating the specimen in hydrogen at 700°C or above to reduce any air-formed film, and then allowing the specimen to attain equilibrium in a highly purified argon atmosphere in the furnace before introducing oxygen. Under these conditions the rate of growth of the total scale was obtained by measuring the increase of weight of the specimen during certain fixed times of oxidation, and the results are shown in Fig. 3. From these results, values for the parabolic rate constant,  $k$ , were obtained for the particular temperatures and the standard plot of  $\log k$  vs. the reciprocal of the absolute temperature is given in Fig. 4.  $k$  is defined by the Pilling and Bedworth equation  $(W/A) = kt^{1/2}$ , where  $W$  is weight gain,  $A$  is area, and  $t$  is time.

Specimens were mounted and sectioned, and the thicknesses of the individual phases were obtained microscopically. The results indicated that in no case, above a temperature of about 625°C, did the scale contain greater than 10 pct by volume of the higher oxides  $Fe_3O_4$  and  $Fe_2O_3$ . Values for the relative thicknesses of the oxides for various times at different temperatures are given in Table I. However, the measurement of the thickness of the two higher oxides could not be made with great precision and more sensitive techniques were devised for the measurement of their growth rates. Values for the increase in thickness of "FeO" are plotted in Fig. 5, and the parabolic rate constant for the growth of this phase approximates that for the growth of the total scale at temperatures above 625°C.

To measure the rate of growth of  $Fe_3O_4$  and  $Fe_2O_3$ , samples of "FeO" and  $Fe_3O_4$  were prepared and these were oxidized in oxygen using a spring balance to determine continuously the rate of increase of weight with time. The results obtained are shown in Figs. 6 and 7, and the rate constants obtained from these results for the oxidation of "FeO" to  $Fe_3O_4$  and  $Fe_3O_4$  to  $Fe_2O_3$  are plotted on Fig. 4.

The main differences between the results obtained in this investigation and previous studies may be summarized as follows:

1—The parabolic rate constant  $k$  in the temperature range 400° to 600°C is lower than that obtained by Stanley and coworkers.<sup>3</sup> It is believed<sup>27</sup> that the discrepancy existing between the true surface area and that calculated from the geometrical dimensions of the specimen led to the higher values for  $k$  calculated by these workers, particularly for the relatively short oxidation times that they employed. In the present investigation the actual surface areas more nearly approach the calculated surface area due to (a) the more highly polished nature of the specimen, and (b) the pre-oxidation anneal in hydrogen at 700°C. The longer oxidation times employed also yield values of  $k$  which more nearly approximate the true value.

2—The inflection in the plot of  $\ln k$  vs.  $1/T$  at about 600°C is associated with the appearance of "FeO" as a stable component of the scale.

3—In the temperature range 600° to 1200°C the variation of  $\ln k$  with  $1/T$  is expressed by a smooth curve, the slope of which changes rapidly at about 800°C, coinciding with the appearance of a finite thickness of  $Fe_2O_3$  in the scale. That is,  $\ln k$  is not a simple linear function of the reciprocal of the

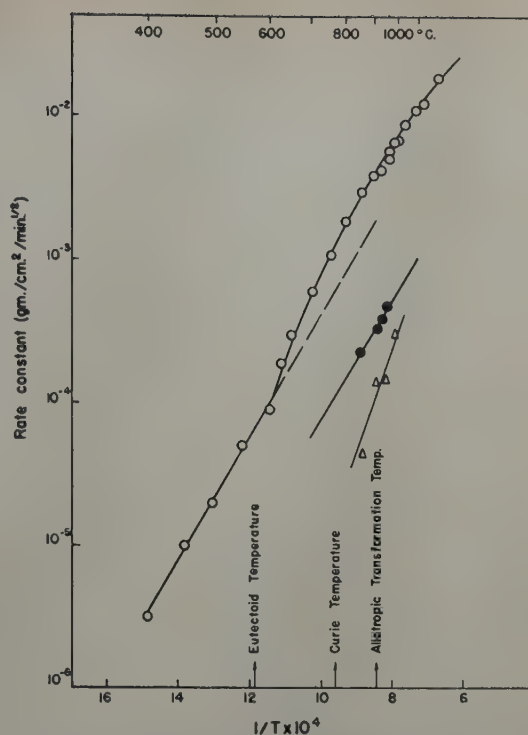


Fig. 4—Plots of the logarithm of the parabolic rate constants for the oxidation of iron, wustite, and magnetite in 1 atm of oxygen vs. the reciprocal of absolute temperature.

absolute temperature, and the so-called inflection previously obtained is not attributable to the phase<sup>3</sup> or magnetic transformation in pure iron. This point will be elaborated later.

4—Microscopic measurements indicate: (a) that at no temperature above about 625°C do the higher oxides,  $Fe_3O_4$  and  $Fe_2O_3$ , form a considerable portion of the scale, (b) the growth of these higher oxides is not linear with time. These results are in direct contradiction to the work of Benard and Coquelle.<sup>1</sup> It is believed that, since the technique employed in the experiments of Benard and Coquelle involves heating the specimen from room temperature to the oxidizing temperature in the oxidizing atmosphere, a thick film is formed during this initial heating period. At the transformation temperature where the metal suffers a contraction, the film may become partially divorced from the metal. If the film is plastic at 910°C, then no rupture will occur and the effect of the partial divorcement of scale and

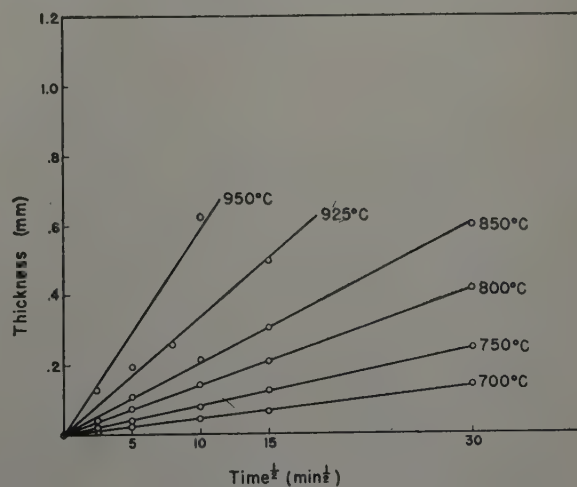


Fig. 5—Rate of growth of "FeO" from microscopic measurement.

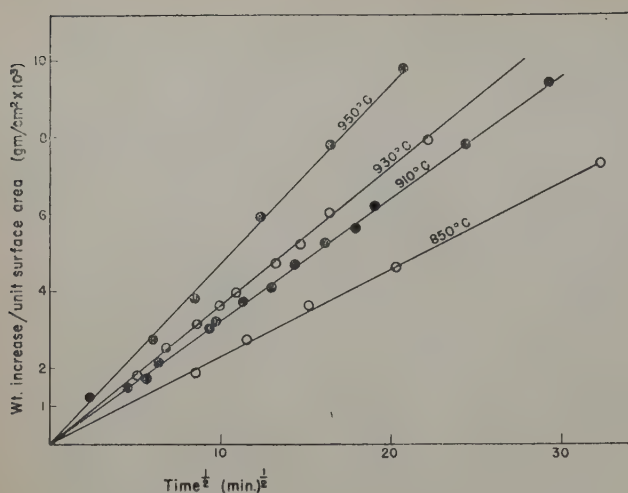


Fig. 6—Parabolic plot for the oxidation of "FeO" in oxygen.

metal will be to reduce the area of contact, thus reducing the supply of iron ions to the scale. This will manifest itself both as a reduction in the total overall rate of oxidation and in the increase in the percentage of the higher oxides in the scale. That is, the percentages of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  will be greater than in a system which is in dynamic equilibrium when the contact between phases is perfect.

Some supporting evidence for the results of the present investigation have been obtained: (a) in the oxidation of iron in water vapor, the overall rate approximates the total oxidation rate in oxygen, but the percentage of  $\text{Fe}_3\text{O}_4$  in the scale remains small until all the iron has been converted to oxide; (b) stress concentration effects at corners and edges of specimens can result in the local separation of scale and metal at some period during oxidation. When this occurs, its effect is to increase locally the amount of the higher oxides in the scale.

5—Results for the rate of oxidation of wüstite and magnetite, Figs. 6 and 7, give a parabolic relationship between gain in weight and time. This shows that the processes are diffusion controlled since an interface reaction controlled process would manifest itself in a linear rate law. The rates of growth derived for the higher oxides under these

Table II. Values for the Parabolic Rate Constants Derived from the Isothermal Oxidation Curves for Fe, "FeO," and  $\text{Fe}_3\text{O}_4$ .

| Temperature,<br>°C                          | <i>k</i>             |
|---------------------------------------------|----------------------|
| Oxidation of FeO                            |                      |
| 950                                         | 4.9x10 <sup>-4</sup> |
| 930                                         | 3.9x10 <sup>-4</sup> |
| 910                                         | 3.3x10 <sup>-4</sup> |
| 850                                         | 2.3x10 <sup>-4</sup> |
| Oxidation of Fe <sub>3</sub> O <sub>4</sub> |                      |
| 800                                         | 4.5x10 <sup>-5</sup> |
| 900                                         | 1.5x10 <sup>-4</sup> |
| 950                                         | 1.3x10 <sup>-4</sup> |
| 988                                         | 3.0x10 <sup>-4</sup> |

| Tempera-<br>ture, °C                      | <i>k</i> (G per Sq<br>Cm per Min <sup>1/2</sup> ) | Tempera-<br>ture, °C | <i>k</i>              |
|-------------------------------------------|---------------------------------------------------|----------------------|-----------------------|
| Oxidation of Fe to Form Multilayer Scales |                                                   |                      |                       |
| 400                                       | 3.4x10 <sup>-8</sup>                              | 800                  | 1.85x10 <sup>-3</sup> |
| 450                                       | 1x10 <sup>-5</sup>                                | 850                  | 3x10 <sup>-3</sup>    |
| 500                                       | 5x10 <sup>-5</sup>                                | 900                  | 3.9x10 <sup>-3</sup>  |
| 600                                       | 9x10 <sup>-5</sup>                                | 930                  | 4.6x10 <sup>-3</sup>  |
| 625                                       | 1.9x10 <sup>-4</sup>                              | 965                  | 5.5x10 <sup>-3</sup>  |
| 650                                       | 3x10 <sup>-4</sup>                                | 1035                 | 9x10 <sup>-3</sup>    |
| 700                                       | 6x10 <sup>-4</sup>                                | 1090                 | 1.1x10 <sup>-2</sup>  |
| 750                                       | 1.1x10 <sup>-3</sup>                              | 1130                 | 1.24x10 <sup>-2</sup> |
|                                           |                                                   | 1200                 | 1.87x10 <sup>-2</sup> |

conditions will be greater than their respective growth rates during the formation of scale, but it will be shown that they do not affect materially the total oxidation rate above 600°C.

### Analysis of the Kinetic Data

Considering oxidation in the range 400° to 570°C in the absence of changing composition limits for the phases  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  with temperature, the plot of  $\ln k$  vs.  $1/T$  will yield a straight line. This results from the fact that the growth rate will be a simple function of the average diffusion coefficient for the components of the scale.

The rate of growth of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  on iron, i.e., below 570°C, is largely dependent upon diffusion in  $\text{Fe}_3\text{O}_4$  since this forms nearly 100 pct of the scale.<sup>1-3</sup> This rate should bear some relationship to the rate of growth of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  on "FeO" where magnetite is again the major component.

The reactions involved, neglecting the formation of  $\text{Fe}_2\text{O}_3$ , are:



On the basis of formation of the same thickness of

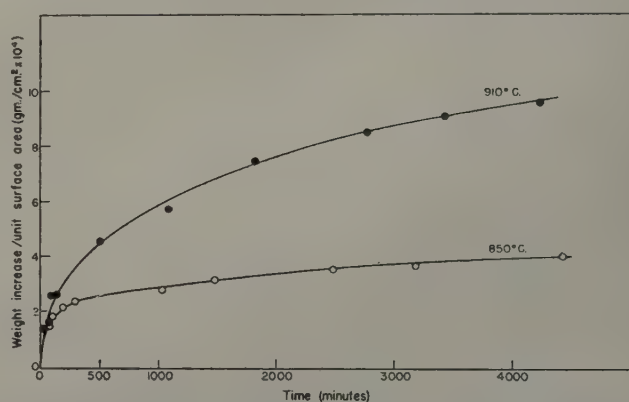


Fig. 7—Curves for the increase of weight with time of magnetite oxidized in oxygen. Approximate values for rate constants are derived from the straight portions of the plot of  $W/A$  vs.  $\text{time}^{1/2}$ .

$\text{Fe}_3\text{O}_4$ , it can be seen that the weight gain in process 1 is four times the weight gain in process 2. Examination of Fig. 4 shows that the extrapolated values for process 1 are four to five times greater than those measured for process 2 at the same temperature. The activation energies are nearly the same.

Above 570°C the picture becomes more complex owing to the wide variation of the composition limits of the "FeO" phase field with temperature. The oxidation process is dependent on diffusion and, in turn, the diffusion rate varies with the concentration gradient in the growing phase. In a phase field with fixed composition limits whose difference is  $\Delta C$ , the only factor affecting diffusion is the actual thickness of the phase,  $\Delta X$ , with respect to those fixed composition limits, and the effect of a changing

$\frac{\Delta C}{\Delta X}$  due to a change in  $\Delta X$  is implied in the normal

parabolic law. When  $\Delta C$  changes also (as in "FeO"), there is another contribution to the rate of diffusion and hence to the rate of growth of the phase. Thus  $\ln k$  will not be a simple function of the reciprocal of the absolute temperature, and the curvature of this relationship is attributed to a changing  $\Delta C$  with temperature in "FeO." That is, for the same thick-



ness of "FeO" formed at different temperatures, there will be an effect on the growth rate due to the fact that the composition limits of the phase will be different, in addition to the normal increase of  $D$ , the average diffusion coefficient, with increase in temperature. Booth<sup>28</sup> has shown that the variation of the diffusion coefficient with concentration does not vitiate the application of the parabolic rate law at any one temperature.

In the absence of interface reaction rate control in the oxidation process, there appears to be no basis for the assumption that phase transformations in the metal can affect the rate of growth. Experiments on the oxidation of manganese<sup>30</sup> show no effect on the parabolic rate constant due to the  $\alpha$  to  $\gamma$  transformation in that metal. However, this does not imply that such effects will not be present under conditions of nonparabolic oxidation.

### Summary

The rates of oxidation of iron in pure oxygen have been determined with good precision over a wide range of temperatures. In general, the overall rates agree with those previously reported, but several systematic differences are noted. Tentative explanations are offered for these differences.

In addition to multilayer scaling rates, the rates of growth of hematite on magnetite and hematite and magnetite on wüstite have been determined. In contradiction with the results of Benard and Coquelle, obtained by micrographic measurements, these rates have been observed to follow a parabolic law rather than a linear law. On the basis of these measurements, it was concluded that the growth of each layer is a diffusion controlled process and that the interface reaction rates may be neglected. The process thus fulfills adequately the assumptions necessary to apply the Valensi<sup>30</sup> treatment of multilayer scaling.

Observing the Kirkendall effects in the growth of each of the oxide phases, with a modification of the Pfeil technique using radioactive silver as inert marker, established the diffusing component for each phase. The process is illustrated schematically in Fig. 8, where the percentages in magnetite are rough values applying at one temperature only.

Below 570°C the overall rate is determined by the growth rate of  $\text{Fe}_3\text{O}_4$ . Above about 620°C, the overall rate seems to be determined principally by the rate of FeO growth. Between 570° and 620°C, as the temperature increases the rate controlling layer changes from  $\text{Fe}_3\text{O}_4$  to FeO, leading to a marked curvature in the  $\log k - 1/T$  plot.

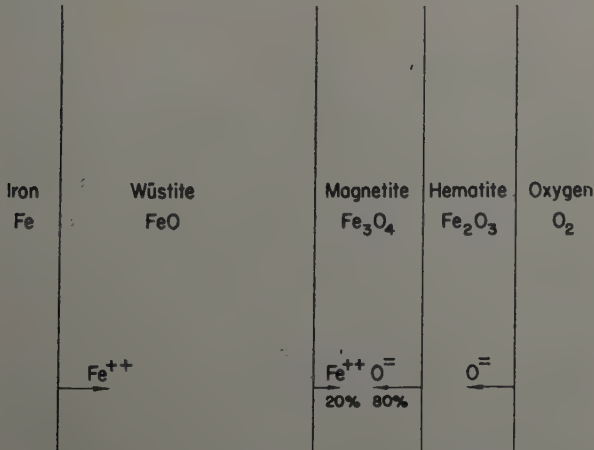


Fig. 8—Schematic diagram of the oxidation process in iron.

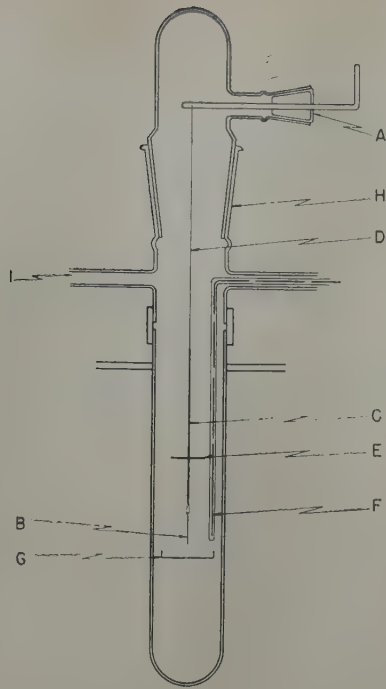


Fig. 9—Design of one furnace unit.

- A—Winch
- B—Specimen
- C—Silica rod
- D—Nylon thread
- E—Silica spokes
- F—Thermocouple
- G—Tray to retain spalled oxide
- H—Ground glass vacuum joint
- I—Connection to gas source.

The parabolic rate constant is a complex function of temperature in the growth of layers such as "FeO" where the range of existence of the phase, as well as the diffusion coefficients, for a given composition depends strongly upon temperature.

The rates of growth of iron oxide layers are rather insensitive to changes in the substrate. There seems to be no great change in the rate of growth of FeO when the substrate changes from  $\alpha$  to  $\gamma$  Fe, and no great change in the rate of growth of  $\text{Fe}_3\text{O}_4$  when the substrate changes from  $\alpha$ Fe to FeO.

### Appendix

#### Experimental Methods and Techniques

**Apparatus:** In these experiments three vertical furnaces were equipped with a glass manifold, constructed so that each furnace could be independently connected to a source of hydrogen, oxygen or argon, or to a vacuum pump.

The design of one of the furnace units is shown, Fig. 9, including the glass winch which served to raise and lower specimens to and from a predetermined position in the furnace.

Each specimen was attached to a silica rod by a platinum hook and the silica rod was in turn attached to the winch by means of nylon thread. Spokes attached to the bottom end of the silica rod prevented the specimen touching the thermocouple sheathing or the wall of the furnace tubing itself.

For some experiments, particularly those concerned with the oxidation of the lower oxides of iron, it was desirable to follow the course of oxidation continuously. This was accomplished by means of a sensitive spring balance. The glass head, containing the winch, of one of the furnaces was extended considerably so that both ends of the spring (which were attached to the winch and to the silica by nylon thread) could be observed with a cathetometer to measure the length of the spring accurately. An alloy of low temperature coefficient of elastic properties, "Nispan C" wire 0.005 in. diam was used for the spring, with a sensitivity of ap-

proximately 0.02 cm per mg. Measurements were reproducible to 0.010 cm, which corresponded to a weight change of 0.5 mg.

Adequate precautions were taken to purify the gases used. The argon was periodically tested by holding a heat-tinted specimen in one of the furnaces in an atmosphere of the gas at 700°C and noting any changes in the appearance of the specimen. The atmosphere was considered satisfactory if no change occurred in the interference color or if a slight reduction in the thickness of the film was indicated.

**Preparation of Specimens and Experimental Procedure:** The iron used in these experiments was Westinghouse Puron. All specimens after cutting and surface grinding were annealed in hydrogen for 24 hr at 900°C. Subsequently, the specimens were hand ground under alcohol on metallographic polishing papers to a fineness of 4/0. They were then washed in alcohol, dried, measured and weighed, rewashed, and then loaded into the furnaces.

The specimens used were approximately  $\frac{3}{4} \times \frac{1}{2} \times 1/10$  in. and their dimensions were accurately measured with a micrometer screw gage so that the total surface area could be computed. A standard chemical balance sufficed for most weighings; however, in those cases where the expected weight increase was relatively small (i.e., for oxidation at low temperatures and for short times), an assay balance was used.

It was believed that the presence of an air-formed film on the surface of the Puron might lead to erroneous results, particularly for the oxidation of specimens at low temperatures and for short times. Consequently, all specimens were given a pre-oxidation anneal in hydrogen at 700°C or above. If the particular oxidation experiment was to be carried out below 700°C, then, following the preliminary hydrogen anneal at 700°C, the specimen was raised to the cool zone, the furnace chamber evacuated, argon admitted, and the furnace allowed to cool to the oxidation temperature desired. Those specimens to be oxidized above 700°C were hydrogen annealed at the oxidation temperature. In all cases, oxygen was not admitted to the furnace until the specimen had reached the equilibrium oxidation temperature in argon. This procedure avoided any spurious effects that might have resulted from oxidation having occurred over a range of temperature in the initial stages.

For the studies on the oxidation of oxides, "FeO" was prepared by oxidizing iron in water vapor. The time of oxidation was calculated so that only a small amount of  $\text{Fe}_3\text{O}_4$  would be produced and this was removed by grinding. "FeO" could also be produced by oxidation of iron in hydrogen-water vapor or carbon monoxide-carbon dioxide mixtures.

The  $\text{Fe}_3\text{O}_4$  was produced by oxidizing iron to constant weight in water vapor.

**Mounting Technique:** Many of the conventional mounting methods were tried; all those involving thermal setting with or without pressure were rejected due to the break up in scale which they frequently occasioned.

The method finally developed and adopted involved making a sandwich of the specimen between two small sheets of polystyrene. A solution of polystyrene in ethylene bromide was used as a cement. After the cement was hardened (in 24 to 36 hr) the protruding ends of the polystyrene were softened and then welded to other pieces of polystyrene to give the mount greater security in the grinding operations. This type of mounting proved adequate for the polishing of the oxides so that thickness measurements might be taken.

**Radioactive Tracer Technique:** The movement of inert markers placed at an interface across which diffusion takes place has been previously studied (Smigelskas and Kirkendall,<sup>31</sup> Da Silva and Mehl<sup>32</sup>). The application of the active silver to the specimen has been described previously. After oxidation, the specimen was mounted, sectioned perpendicular to the flat face, and polished. The polished edge was placed in in-

timate contact with a spectrographic or No-Screen X-ray plate. After a sufficient period of exposure, the plate was developed, and the separation of the streaks due to the active silver on either face of the sample was measured.

### Acknowledgments

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# Effects of Tungsten or Molybdenum Upon the Alpha-Beta Transformation and Gamma Precipitation In Cobalt-Chromium Alloys

by E. E. Fletcher and A. R. Elsea

This paper describes a metallographic investigation of the influence of tungsten or molybdenum additions upon the transformation and precipitation reactions occurring in Co-rich Co-Cr alloys. It is shown that tungsten has little effect upon the  $\alpha$ - $\beta$  transformation temperature range, while molybdenum tends to raise it. Both elements tend to promote the formation of  $\gamma$  phase, molybdenum being more potent in this respect than tungsten.

HIGH temperature alloys, that is, alloys which have load-carrying ability at elevated temperatures, have been developed at an increasing rate during the past few years. This has resulted from the requirements in the design of modern aircraft engines. Although many alloys of this type are available, they have been developed on an empirical basis. Metallurgists do not have a clear understanding of the phases or structures that are responsible for these high temperature properties.

In order to determine why these alloys possess this particular ability, a project was started at Battelle Memorial Institute with the object of learning more about the fundamental factors which promote high temperature strength in alloys. This study was to include a correlation of microstructure and the high temperature properties of Vitallium, an alloy which is widely used for high temperature service. Vitallium is a complex material both from the standpoint of composition and microstructure. Consequently, it was necessary to obtain informa-

tion regarding the phase relationships in this alloy.

The Co-Cr binary diagram was determined as the first phase of this investigation.<sup>1</sup> A second paper described the effects of iron, nickel, or nitrogen on the reactions occurring in the Co-rich end of this system.<sup>2</sup> The present paper covers a continuation of this investigation in which the effects of tungsten or molybdenum on the reactions occurring in Co-rich, Co-Cr-base alloys were determined.

## Preparation of Test Materials

Two series of ternary Co-Cr-base alloys, representing Co-Cr ratios of 80:20 and 68:32

$\left( \frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20 \text{ and } 32 \right)$ , were prepared containing

up to 6 pct W and up to 12 pct Mo.

Melting stock consisted of electrolytic Co, electrolytic Cr, 99.9 pct pure W, and 99.9 pct pure Mo. Table I lists the chemical analyses of these materials.

The melting furnace was a vertical porcelain tube

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<sup>2</sup> A. R. Elsea and C. C. McBride: The Effects of Nitrogen, Iron, or Nickel Upon the Alpha-Beta Transformation and Gamma Precipitation in Cobalt-Chromium Alloys. *Trans. AIME* (1950) 188, p. 154; *JOURNAL OF METALS* (January 1950).

Table I. Chemical Analyses of Melting Stock

| Element                       | Electrolytic Co |        | Electrolytic Cr | W*       | Mo*       |
|-------------------------------|-----------------|--------|-----------------|----------|-----------|
|                               | Lot 5           | Lot 7  |                 |          |           |
| C                             | 0.02            | 0.03   | 0.02            |          | 0.003 max |
| Si                            | <0.01           | <0.005 | 0.08            |          |           |
| Fe                            | 0.08            | 0.21   | 0.048           |          | 0.005 max |
| Ni                            | 0.55            | 0.24   |                 |          |           |
| S                             | 0.006           | <0.005 |                 |          |           |
| Co                            | Bal.            | Bal.   |                 |          |           |
| Cr                            |                 |        | Bal.            |          |           |
| W                             |                 |        |                 | 99.9+    |           |
| Mo                            |                 |        |                 |          | 99.9+     |
| O <sub>2</sub>                |                 |        | 1.23            |          |           |
| N <sub>2</sub>                |                 |        | 0.026           |          |           |
| H <sub>2</sub>                |                 |        | 0.0166          |          |           |
| R <sub>2</sub> O <sub>3</sub> |                 |        |                 | 0.02 max |           |

\* Typical analysis from supplier.

heated by a tubular Globar element and was designed for controlled-atmosphere melting. A purified argon atmosphere was used in all of the melting operations. High purity tank argon (99.87 or 99.92 pct argon) was passed through magnesium perchlorate to remove the moisture and then through a container of titanium-metal granules heated to 750°C for removal of nitrogen and oxygen.

The 200-g charges were melted in Alundum thimble crucibles which absorbed chromium oxide and tended to deoxidize the melts. Close-fitting graphite sleeves were used to support the crucibles during charging, melting, and casting. The alloys picked up about 0.1 pct C during melting. However, during subsequent homogenization, the carbon was usually reduced to within the limits of 0.01 to 0.05 pct.

Prior to casting, the melts were briefly stirred and then centrifugally cast into investment molds yielding four rectangular bars, 3/16 x 1/4 in. x about 4 1/2 in. long.

The cast bar stock was homogenized for 75 to 80 hr at 1260°C, in an atmosphere of purified argon, and subsequently water quenched. Metallographic examination of the homogenized stock showed that it was free from microsegregation. Chips were obtained from the tops and bottoms of the homogenized bars for chemical analyses, the results of which are shown in Table II for the tungsten alloys, and in Table III for the molybdenum alloys.

### Transformation Studies

**Preliminary Aging Tests:** Specimens of the homogenized Co-Cr-W and Co-Cr-Mo alloys were heat treated in purified argon for 100 hr at temperatures in the range of 700° to 1175°C, and water quenched to room temperature. Temperatures at 25°C intervals, within the above-mentioned temperature range, were selected for the heat treatments. The specimens were then examined metallographically to determine the phases present. Throughout this investigation, the phases were identified metallographically using the etching reagents and procedures described in an earlier paper.<sup>1</sup> No new phases were encountered in these systems. The results of this examination, plotted as a function of temperature and composition, gave an indication of the effects of the third element upon the reactions occurring in these alloys.

The  $\alpha$ - $\beta$  transformation in these alloys is very sluggish, presumably because the energy change involved in this transformation is small. Consequently, the results obtained from these tests show only trends and serve to block in regions for further study. Later in this paper a description is given of

an experimental technique used to eliminate the factor of sluggishness.

Large amounts of a precipitate were found in the

high molybdenum alloys where  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 32$ .

Microscopic examination suggested that the precipitate might be  $\gamma$  phase ( $\text{Co}_2\text{Cr}_3$ ). This was verified by X-ray diffraction studies. It was also observed that in the high molybdenum alloys the interplanar spacings of  $\alpha$ ,  $\beta$ , and  $\gamma$  were expanded about 1 to 1 1/2 pct over those of a Mo-free alloy. Hence, it is concluded that in the Co-Cr-Mo alloys, the molybdenum is in solution in both  $\gamma$  and the two Co-rich terminal solid solutions,  $\alpha$  and  $\beta$ .

Difficulties were encountered in identifying the matrix structures of the 7.92 and 11.65 pct Mo alloys

with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} =$  approximately 32. These two

alloys, when aged at 1025°C and below, showed massive  $\gamma$  and also clouds of fine  $\gamma$  precipitate which masked the matrix and prevented metallographic identification. When these alloys were pre-aged at 1100°C for 60 hr and then aged at 1025°C and below, the  $\gamma$  phase coming out of solution during the second aging treatment tended to deposit on the massive  $\gamma$  particles already present. This pre-aging treatment resulted in a substantial increase in size and decrease in number of precipitated particles present when the alloys were aged at temperatures below 1025°C. Thus, the matrix phases could be identified metallographically, but the relative amounts could not be estimated.

On the basis of these preliminary tests, the approximate  $\alpha$ - $\beta$  transformation range for the alloy containing 7.92 pct Mo appears to be from 960° to 990°C.; the range for the 11.65 pct alloy is approximately 980° to 1010°C.

**Accurate Determination of the Transformation:** All of the preliminary or blocking-in aging treatments on the W and Mo-bearing ternary alloys were carried out on stock which had previously been quenched from the homogenizing temperature. This

Table II. Chemical Analyses of Co-Cr-W Ternary Alloys

| Designation | Alloy  | Composition, Pct |      |      |      |                |      |      | Actual Cr x 100<br>Co + Cr |
|-------------|--------|------------------|------|------|------|----------------|------|------|----------------------------|
|             |        | Co*              | Cr   | W    | C    | N <sub>2</sub> | Fe†  | Ni†  |                            |
| DA          | Top    | 79.0             | 19.5 | 1.00 | 0.02 | 0.004          | 0.09 | 0.38 | 19.8                       |
|             | Bottom | 79.2             | 19.2 | 1.10 |      |                |      |      | 19.5                       |
| DAA         | Top    | 79.0             | 19.3 | 1.19 | 0.03 | 0.003          | 0.24 | 0.27 | 19.6                       |
|             | Bottom | 78.8             | 19.5 | 1.19 |      |                |      |      | 19.8                       |
| DB          | Top    | 77.3             | 19.0 | 3.03 | 0.01 | 0.004          | 0.19 | 0.48 | 19.7                       |
|             | Bottom | 77.4             | 18.9 | 3.00 |      |                |      |      | 19.6                       |
| DBC         | Top    | 77.1             | 19.7 | 2.69 | 0.02 | 0.004          |      |      | 20.4                       |
|             | Bottom | 77.2             | 19.6 | 2.76 |      |                | 0.12 | 0.33 | 20.2                       |
| DC          | Top    | 75.0             | 18.5 | 5.93 | 0.02 | 0.005          | 0.08 | 0.47 | 19.8                       |
|             | Bottom | 75.0             | 18.5 | 5.95 |      |                |      |      | 19.8                       |
| DCA         | Top    | 75.2             | 18.3 | 5.96 | 0.02 | 0.003          | 0.26 | 0.29 | 19.6                       |
|             | Bottom | 75.1             | 18.4 | 5.94 |      |                |      |      | 19.7                       |
| DD          | Top    | 67.1             | 31.3 | 1.04 | 0.02 | 0.011          | 0.11 | 0.45 | 31.8                       |
|             | Bottom | 67.3             | 31.0 | 1.08 |      |                |      |      | 31.5                       |
| DDA         | Top    | 67.1             | 31.6 | 0.96 | 0.01 | 0.005          | 0.15 | 0.21 | 32.0                       |
|             | Bottom | 66.9             | 31.7 | 1.04 |      |                |      |      | 32.2                       |
| DDB         | Top    | 66.6             | 31.9 | 1.05 | 0.02 | 0.005          | 0.24 | 0.23 | 32.4                       |
|             | Bottom | 66.9             | 31.6 | 1.01 |      |                |      |      | 32.1                       |
| DE          | Top    | 65.6             | 30.8 | 3.04 | 0.01 | 0.004          | 0.11 | 0.39 | 31.9                       |
|             | Bottom | 65.7             | 30.7 | 3.07 |      |                |      |      | 31.8                       |
| DEC         | Top    | 65.5             | 31.1 | 2.95 | 0.03 | 0.013          | 0.21 | 0.20 | 32.2                       |
|             | Bottom | 65.7             | 31.0 | 2.89 |      |                |      |      | 32.1                       |
| DF          | Top    | 64.0             | 30.0 | 5.46 | 0.04 | 0.012          | 0.12 | 0.39 | 31.9                       |
|             | Bottom | 64.5             | 29.4 | 5.58 |      |                |      |      | 31.3                       |

\* By difference.

† Spectrographic estimates,  $\pm 25$  pct approximately.



Table III. Chemical Analyses of Co-Cr-Mo Ternary Alloys

| Designation | Alloy  | Composition, Pct |      |      |      |                |      |      | Actual<br>Cr x 100<br>Co + Cr |
|-------------|--------|------------------|------|------|------|----------------|------|------|-------------------------------|
|             |        | Co*              | Cr   | Mo   | C    | N <sub>2</sub> | Fe†  | Ni†  |                               |
| MA          | Top    | 79.0             | 19.6 | 0.95 | 0.02 | 0.005          | 0.10 | 0.38 | 19.9                          |
|             | Bottom | 79.3             | 19.3 | 0.95 |      |                |      |      | 19.6                          |
| MAB         | Top    | 79.5             | 19.3 | 0.79 | 0.01 | 0.002          | 0.18 | 0.21 | 19.5                          |
|             | Bottom | 79.2             | 19.6 | 0.82 |      |                |      |      | 19.8                          |
| ME          | Top    | 76.3             | 19.1 | 4.00 | 0.02 | 0.007          | 0.20 | 0.37 | 20.0                          |
|             | Bottom | 76.4             | 18.9 | 4.08 |      |                |      |      | 19.8                          |
| MBD         | Top    | 75.9             | 19.8 | 3.94 | 0.01 | 0.008          | 0.15 | 0.20 | 20.7                          |
|             | Bottom | 75.6             | 20.1 | 3.92 |      |                |      |      | 21.0                          |
| MBE         | Top    | 75.9             | 19.7 | 3.92 | 0.03 | 0.006          | 0.23 | 0.21 | 20.6                          |
|             | Bottom | 75.9             | 19.7 | 3.90 |      |                |      |      | 20.6                          |
| MC          | Top    | 73.7             | 17.7 | 7.93 | 0.05 | 0.003          | 0.21 | 0.39 | 19.4                          |
|             | Bottom | 73.8             | 17.8 | 7.73 |      |                |      |      | 19.4                          |
| MCA         | Top    | 73.1             | 18.5 | 7.79 | 0.02 | 0.003          | 0.36 | 0.27 | 20.2                          |
|             | Bottom | 73.3             | 18.2 | 7.85 |      |                |      |      | 19.9                          |
| MD          | Top    | 69.6             | 17.8 | 11.9 | 0.05 | 0.007          | 0.28 | 0.40 | 20.4                          |
|             | Bottom | 70.3             | 17.1 | 11.9 |      |                |      |      | 19.6                          |
| MDA         | Top    | 69.9             | 17.9 | 11.5 | 0.02 | 0.003          | 0.40 | 0.24 | 20.4                          |
|             | Bottom | 69.9             | 17.9 | 11.5 |      |                |      |      | 20.4                          |
| ME          | Top    | 67.6             | 30.9 | 0.68 | 0.04 | 0.017          | 0.28 | 0.48 | 31.4                          |
|             | Bottom | 67.6             | 30.9 | 0.71 |      |                |      |      | 31.4                          |
| MEA         | Top    | 67.1             | 31.4 | 0.95 | 0.01 | 0.008          | 0.27 | 0.23 | 31.9                          |
|             | Bottom | 66.9             | 31.6 | 0.97 |      |                |      |      | 32.1                          |
| MF          | Top    | 66.2             | 29.7 | 3.42 | 0.07 | 0.017          | 0.23 | 0.36 | 31.0                          |
|             | Bottom | 66.0             | 29.7 | 3.63 |      |                |      |      | 31.0                          |
| MG          | Top    | 63.1             | 28.3 | 7.81 | 0.05 | 0.021          | 0.29 | 0.43 | 31.0                          |
|             | Bottom | 63.1             | 28.1 | 8.04 |      |                |      |      | 30.8                          |
| MGA         | Top    | 62.5             | 29.0 | 7.90 | 0.02 | 0.004          | 0.33 | 0.21 | 31.7                          |
|             | Bottom | 62.5             | 29.1 | 7.79 |      |                |      |      | 31.8                          |
| MH          | Top    | 60.0             | 27.3 | 11.6 | 0.09 | 0.008          | 0.42 | 0.56 | 31.3                          |
|             | Bottom | 60.1             | 27.1 | 11.7 |      |                |      |      | 31.1                          |

\* By difference.

† Spectrographic estimates,  $\pm 25$  pct approximately.

treatment produced prior structures of  $\alpha$  plus a martensitic-type  $\beta$ . Because the  $\alpha$ - $\beta$  reaction is sluggish, equilibrium conditions are not attained in these alloys in 100 hr of aging. The results of reaction-rate tests made during the early work on Co-Cr binary alloys<sup>1</sup> indicated that 30 days or more would be required to reach equilibrium in the 80 pct Co-20 pct Cr alloy at 808°C. It is certainly not feasible to treat specimens isothermally for this length of time in determining phase diagrams.

If an aging time less than that required to attain equilibrium is used, the transformation temperature will appear to be lower or higher than the equilibrium values depending on whether the prior structures of the specimens were  $\alpha$  or  $\beta$ , respectively. However, this factor of undercooling or overheating can be eliminated, while still using relatively short aging times, if the following procedure is used:

Specimens with all- $\beta$  and all- $\alpha$  structures are aged simultaneously at various temperatures in and near the transformation temperature range, as determined by the preliminary blocking-in tests. Metallographic examination shows the phases forming in each specimen at particular aging temperatures; consequently, those phases which are in equilibrium at a given temperature are determined. Thus, by eliminating the factor of sluggishness, both the upper and lower limits of the  $\alpha$ - $\beta$  transformation range for each alloy are defined quite accurately.

The simultaneous aging of all- $\alpha$  and all- $\beta$  specimens in order to determine the limits of the transformation will hereafter be referred to as the "up-and-down" treatment. This is carried out as follows:

Small specimens are cut from the bar stock that has been previously transformed to  $\beta$ . All- $\alpha$  specimens are obtained by pretreating homogenized stock for a minimum of 3 hr at 1200°C in an argon atmosphere; these specimens are transferred directly from the pretreating furnace to the aging furnace. As the transfer is made, the cold  $\beta$  specimen is placed in the hot Alundum boat containing the  $\alpha$  specimen. A

stainless steel block, heated to 1200°C, is used during the transfer to conserve heat in the Alundum boat and the  $\alpha$  specimen, so that the temperature of the  $\alpha$  specimen does not drop below the aging temperature. The pair of specimens is aged isothermally in an argon atmosphere for 100 hr at the temperature being investigated, and then water quenched.

The first step in the up-and-down treatment is the preparation of specimens with  $\beta$  structures. The preliminary blocking-in tests indicated that all- $\beta$  or  $\beta$ + $\gamma$  structures could be obtained in 7 of the 14 alloys studied by aging for 100 hr at particular temperatures. Bars of these alloys were aged for 150 hr at the selected temperatures to insure completion of the transformation to  $\beta$ . The predominately  $\beta$  structures of these bars were verified by metallographic examination of the top and bottom of each bar. The two alloys which required double-aging treatments to agglomerate the  $\gamma$  phase were not amenable to the up-and-down type of test, so no attempts were made to produce  $\beta$  structures in these alloys.

In the preliminary tests, 100-hr aging treatments failed to produce all- $\beta$  or  $\beta$ + $\gamma$  structures in five of the alloys (1.05, 3.02, and 5.94 pct W, and 0.95 and

4.04 pct Mo with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = \text{approximately } 20$ ).

This undoubtedly resulted from the sluggishness of the transformation at relatively low temperatures. All of the alloys mentioned contained a minimum of about 2 to 5 pct  $\alpha$  after aging, with the exception of the 5.94 pct W alloy; in this, the  $\alpha$  structure predominated at all of the aging temperatures.

Tests were made to determine whether cold working prior to aging would speed up the transformation from  $\alpha$  to  $\beta$ . It was found that cold reducing 15 pct before aging at the appropriate temperatures for 75 hr resulted in structures which were essentially  $\beta$  phase in the five sluggish alloys. Consequently,  $\beta$  stock for these alloys was prepared in this manner. To eliminate the possible influence of prior history on the transformation, the all- $\alpha$  specimens were also prepared from cold-worked stock.

After metallographic examination of the up-and-down test specimens, a comparison of the prior structures was made with those observed after aging.

Table IV. Summary of  $\alpha$ - $\beta$  Transformation Data for Co-Cr Alloys with Ternary Additions of W and Mo

| Alloy | W, Pct | Mo, Pct | Actual<br>Cr x 100<br>Co + Cr | Experimental<br>Trans-<br>formation,<br>°C | Correction, °C |                | Corrected*<br>Trans-<br>formation,<br>°C |
|-------|--------|---------|-------------------------------|--------------------------------------------|----------------|----------------|------------------------------------------|
|       |        |         |                               |                                            | Lower<br>Limit | Upper<br>Limit |                                          |
| DAA   | 1.19   |         | 19.7                          | 797-835                                    | +5             | +5             | 802-840                                  |
| DBC   | 2.72   |         | 20.3                          | 800-840                                    | -4             | -4             | 796-836                                  |
| DCA   | 5.95   |         | 19.6                          | 813-850                                    | +7             | +7             | 820-857                                  |
| DD    | 1.06   |         | 31.7                          | 916-931                                    | +2             | +2             | 918-933                                  |
| DE    | 3.06   |         | 31.9                          | 919-941                                    | +1             | +1             | 920-942                                  |
| DF    | 5.52   |         | 31.6                          | 891-913                                    | +3             | +3             | 894-916                                  |
| MAB   |        | 0.80    | 19.7                          | 807-842                                    | +5             | +5             | 812-847                                  |
| MBE   |        | 3.91    | 20.6                          | 845-883                                    | -9             | -9             | 836-874                                  |
| MC    |        | 7.83    | 19.4                          | 903-933                                    | +11            | +11            | 914-944                                  |
| MD    |        | 11.9    | 20.0                          | 978-1015                                   | 0              | 0              | 978-1015                                 |
| ME    |        | 0.70    | 31.4                          | 909-926                                    | +4             | +4             | 913-930                                  |
| MF    |        | 3.52    | 31.0                          | 935-949                                    | +7             | +6             | 942-955                                  |
| MG    |        | 7.92    | 30.9                          | 960-990                                    | +8             | +7             | 968-997                                  |
| MH    |        | 11.65   | 31.2                          | 980-1010                                   | +5             | +5             | 985-1015                                 |

\* Corrected to  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20.0$  or 32.0.

This showed which phases were forming at the aging temperature. Knowledge of the phases in equilibrium followed directly from a comparison of the new phases forming in each specimen of a pair aged at any one temperature. Knowing which phases are in equilibrium at a given temperature permits locating the  $\alpha$ - $\beta$  transformation range with respect to this temperature.

For each of the alloys investigated, a plot was made of the up-and-down structural data as a function of the isothermal aging temperature. For convenience, the amounts of  $\alpha$  present in the specimens with both  $\alpha$  and  $\beta$  prior structures were plotted, as well as the amount corresponding to the average or equilibrium structure. For each alloy, the temperatures represented by the intersection of a straight line passed through the equilibrium points with the ordinates corresponding to 0 and 100 pct  $\alpha$  have been taken as the lower and the upper limits, respectively, of the transformation range. These temperatures are summarized in Table IV.

The alloys with the two highest molybdenum contents and with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 32$  were not amenable to the up-and-down type of treatment, because double-aging treatments were necessary in those alloys to permit identification of the matrix phases. Consequently, the data for these two alloys were obtained from only the preliminary tests in which the double-aging treatments were used.

It was intended that these studies would be made on alloys with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20.0$  and 32.0. As shown in the chemical analyses in Tables II and III and summarized in Table IV, the alloys did not exactly meet these requirements. Corrections were applied

to the experimental data to adjust for the slight variations in chromium content.

These corrections were determined in the following manner: The value of  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}}$  was calculated for each alloy. (These values are given in Table IV.) Then, by referring to the Co-Cr binary diagram,<sup>1</sup> the transformation temperature of a binary alloy with that chromium content was noted. The difference between this temperature and the transformation temperature for the 20.0 or 32.0 pct Cr alloy, as the case might be, was taken as the correction to be applied algebraically to the transformation temperature of the ternary alloy under consideration. As an example, consider alloy DAA

(Table IV) which has a value of  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 19.7$ .

The limits of the  $\alpha + \beta$  field of a binary alloy with 19.7 pct Cr are 5°C lower than the limits for one containing 20.0 pct Cr. Then 5°C is added to the experimental transformation limits for alloy DAA to give the corrected transformation range shown in the last column in Table IV.

In the same manner the temperatures of the individual up-and-down tests and the preliminary aging tests were corrected so that the observed

structures represent alloys with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} =$  exactly

20 and 32. The corrected values are plotted in Figs. 1 to 4, showing the effect of tungsten or molybdenum upon the  $\alpha + \beta$  temperature range in these alloys. After these differences in chromium content are compensated for, the data more clearly show the

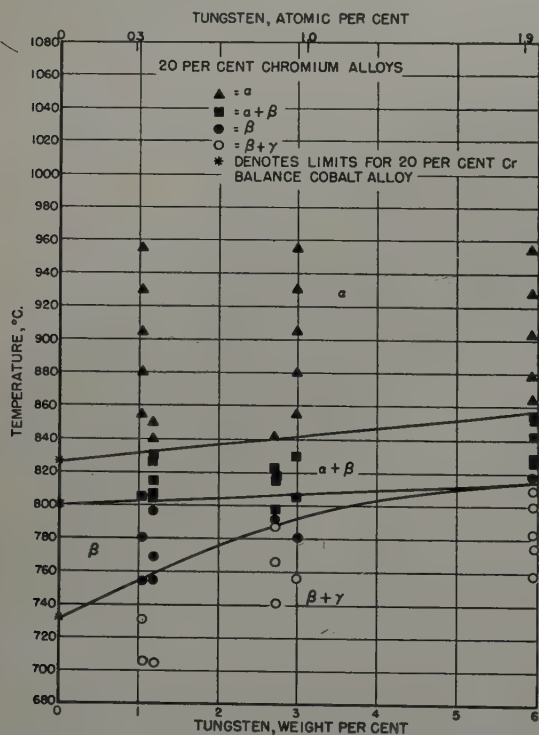


Fig. 1—Effect of tungsten on alpha plus beta temperature range and gamma precipitation in Co-Cr-W alloys with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20.0$ .

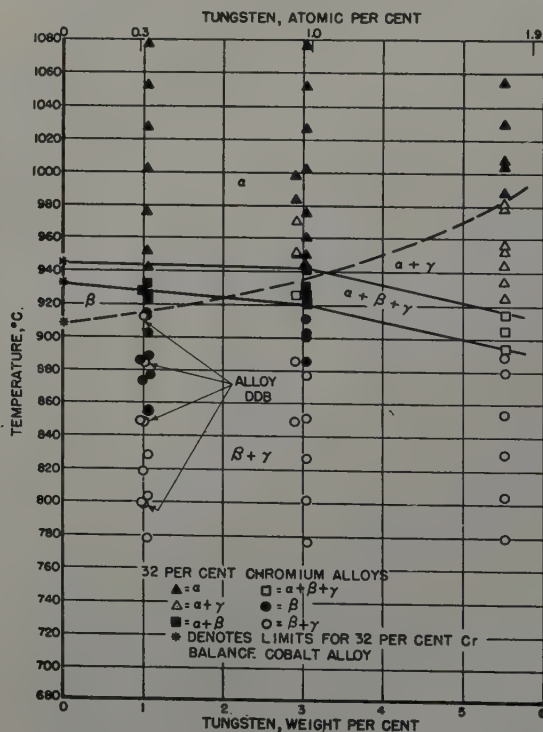


Fig. 2—Effect of tungsten on alpha plus beta temperature range and gamma precipitation in Co-Cr-W alloys with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 32.0$ .



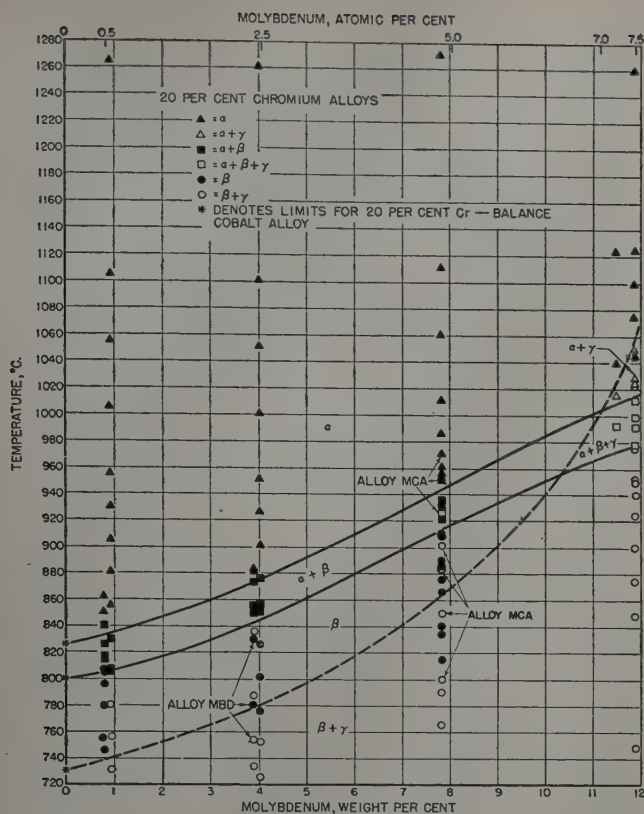


Fig. 3—Effect of molybdenum on alpha plus beta temperature range and gamma precipitation in Co-Cr-Mo alloys with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20.0$ .

effects of tungsten and molybdenum upon the transformation.

It would be desirable to make corrections also for the small amounts of nitrogen, iron, and nickel present in these alloys as impurities, inasmuch as the effects of these elements have been determined.<sup>2</sup> However, these additional corrections were not made for reasons covered in the discussion.

**Gamma Precipitation:** All of the preliminary and up-and-down aged specimens were repolished and etched so that  $\gamma$  phase, if present, could be detected metallographically. Additional aging tests were required for those alloys in which the  $\alpha$ - $\beta$  transformation and the limit of  $\gamma$  solubility are found in different temperature ranges. All of these supplementary tests were made on homogenized stock cold worked to a reduction of 15 pct to accelerate the precipitation of  $\gamma$  phase. The first specimens were aged for 50 hr; all others were aged 100 hr so that the data obtained from these are comparable with the results from those up-and-down specimens which had been cold worked.

Corrections for variations in chromium were applied to these data, using the method described earlier in this paper. These temperatures are summarized in Table V and indicate the temperature at which  $\gamma$  starts to precipitate in each alloy. The corrected data are also plotted in Figs. 1 through 4.

Thus, Figs. 1 through 4 show the influence of tungsten and molybdenum on both the  $\alpha$ - $\beta$  transformation and the precipitation of  $\gamma$  in Co-Cr alloys with

$$\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20 \text{ and } 32.$$

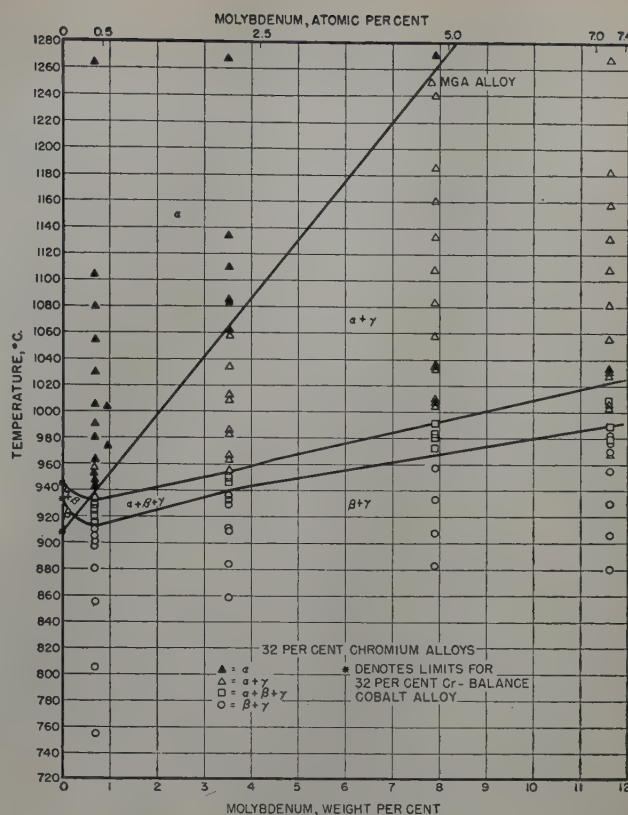


Fig. 4—Effect of molybdenum on alpha plus beta temperature range and gamma precipitation in Co-Cr-Mo alloys with  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 32.0$ .

### Discussion of Results

As mentioned earlier in this paper, it would have been desirable to apply corrections to the data to compensate for the traces of iron, nickel, and nitrogen present as impurities. However, when attempts were made to apply such corrections, inconsistent results were obtained. For example, in some cases after these corrections were made, the lower limit of the  $\alpha$ + $\beta$  region was above the upper limit. This, of course, is impossible. One explanation for this might be the inaccuracy of the ternary diagrams at these small percentages (traces) of the third element. It is also possible that interactions occur between the traces of iron, nickel, or nitrogen and the molybdenum or tungsten present in the alloys being studied, in which case the correction factors obtained from the ternary diagrams would not apply. Consequently, in Figs. 1 through 4 no corrections have been made for impurities in the alloys.

In the up-and-down tests on one of the molybde-

num alloys (alloy MF with 3.52 pct Mo and  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}}$

$= 31.0$ ), two pairs of specimens appeared to have inconsistent structure ratings. These two pairs were treated isothermally at temperatures 2°C apart, the second test intended as a check of the first. Normally after an up-and-down aging treatment in the  $\alpha$ - $\beta$  transformation range for each pair, the specimen with an  $\alpha$  prior structure contains more  $\alpha$  than the one which had a  $\beta$  prior structure. Under ideal conditions in which equilibrium is attained, the two would have the same amount of a given phase. In these tests, after aging, the specimens which were

Table V. Summary of  $\gamma$ -Solubility Data for Co-Cr Alloys with Ternary Additions of W and Mo

| Alloy | W, Pct | Mo, Pct | Actual Cr x 100 Co + Cr | Experimental Limit of Solubility, °C | Correction, °C | Corrected Limit of Solubility,* °C |
|-------|--------|---------|-------------------------|--------------------------------------|----------------|------------------------------------|
| DAA   | 1.19   |         | 19.7                    | 744                                  | +6             | 750                                |
| DBC   | 2.72   |         | 20.3                    | 795                                  | -8             | 787                                |
| DCA   | 5.95   |         | 19.6                    | 805                                  | +9             | 814                                |
| DD    | 1.06   |         | 31.7                    | 850                                  | +3             | 853                                |
| DDA   | 1.00   |         | 32.1                    | 886                                  | -1             | 885                                |
| DDB   | 1.03   |         | 32.2                    | 917                                  | -2             | 915                                |
| DE    | 3.06   |         | 31.9                    | 882                                  | +1             | 883                                |
| DEC   | 2.92   |         | 32.1                    | 980                                  | -1             | 979                                |
| DF    | 5.52   |         | 31.6                    | 980                                  | +4             | 984                                |
| MA    |        | 0.95    | 19.7                    | 780                                  | +6             | 786                                |
| MAB   |        | 0.80    | 19.7                    | 740                                  | +6             | 746                                |
| MB    |        | 4.04    | 19.9                    | 760                                  | +2             | 762                                |
| MBD   |        | 3.93    | 20.8                    | 790                                  | -20            | 770                                |
| MBE   |        | 3.91    | 20.6                    | 857                                  | -15            | 842                                |
| MC    |        | 7.83    | 19.4                    | 790                                  | +16            | 806                                |
| MCA   |        | 7.82    | 20.0                    | >925                                 | 0              | >925                               |
| MD    |        | 11.9    | 20.0                    | 1060                                 | 0              | 1060                               |
| MDA   |        | 11.5    | 20.4                    | 1030                                 | -10            | 1020                               |
| ME    |        | 0.70    | 31.4                    | 930                                  | +5             | 935                                |
| MEA   |        | 0.96    | 32.0                    | <970                                 | 0              | <970                               |
| MF    |        | 3.52    | 31.0                    | 1051                                 | +9             | 1060                               |
| MG    |        | 7.92    | 30.9                    | 1250                                 | +10            | 1260                               |
| MGA   |        | 7.85    | 31.7                    | >1250                                | +3             | >1253                              |
| MH    |        | 11.65   | 31.2                    | >1260                                | +7             | >1267                              |

\* Corrected to  $\frac{\text{Cr} \times 100}{\text{Co} + \text{Cr}} = 20.0$  or  $32.0$ .

formerly  $\alpha$  contained much less  $\alpha$  than did the specimens which were formerly  $\beta$ . However, it was found that in each instance the specimen which was formerly  $\alpha$  contained much less  $\gamma$  after aging than did the specimen which was formerly  $\beta$  phase. This large differential in the amount of  $\gamma$  phase which precipitated means that the composition of the matrix phase for the two specimens of each pair was different. Since the  $\gamma$  phase is rich in chromium ( $\text{Co}_2\text{Cr}_3$ ), the matrix of the specimen with the most  $\gamma$  precipitate was lower in chromium content than that of the other. The Co-Cr binary diagram shows that as the chromium content is lowered, the transformation temperature range is also lowered. Thus, since the two specimens were aged at the same temperature, the specimen which was formerly  $\alpha$  was lower in its transformation range, and hence contained more  $\beta$ .

One of the objectives of this investigation was to learn the reason for the inconsistent high temperature mechanical properties of Vitallium. Erratic data obtained while determining the temperatures at which  $\gamma$  starts to precipitate in the W and Mo-bearing ternary alloys may be associated with these inconsistent properties. For example, in alloys of nominally the same composition, the temperature at which the first metallographic trace of  $\gamma$  was observed varied by as much as  $120^\circ\text{C}$ . These data have been summarized in Table V.

In Figs. 1 through 4, the  $\gamma$  precipitation studies at most of the concentration levels of the ternary addition element were made on two and occasionally three alloys of approximately the same composition. In every instance, the up-and-down tests were made on only one of the alloys at a given concentration level. In plotting the results of the preliminary, up-and-down, and  $\gamma$ -precipitation aging tests, the abscissas represent the ternary alloy content of that

alloy actually used for a specific heat treatment. In some instances, the alloy contents are so close as to lead to confusion of structural data of one alloy with that of another. In such instances, one of the alloys has been identified by the code used in the tables of chemical analyses and in the tables summarizing the results of the transformation and the  $\gamma$ -precipitation studies.

For example, in Fig. 3, three alloys are represented with approximately 4 pct Mo, one at 4.04 pct and others at 3.93 and 3.91 pct. Information obtained using the alloy containing 3.93 pct Mo has been labeled "alloy MBD" to distinguish it from data pertaining to the alloy with 3.91 pct Mo (alloy MBE). As shown in the figure and summarized in Table V, the temperature at which  $\gamma$  starts to precipitate in these three alloys varies considerably. It ranges from about  $760^\circ\text{C}$  for alloy MB (4.04 pct Mo) and  $770^\circ\text{C}$  for alloy MBD (3.93 pct) to about  $840^\circ\text{C}$  for alloy MBE (3.91 pct).

Undoubtedly these variations in  $\gamma$ -precipitation characteristics are influenced either by trace elements (impurities) or by prior mechanical or thermal history. The factors responsible for these variations in the ternary alloys may also be responsible for the inconsistent mechanical properties of Vitallium, because of the influence of  $\gamma$  precipitation on mechanical properties. It is planned to study this more thoroughly in the next phase of this investigation.

### Summary

Results of this investigation show that tungsten has little effect upon the  $\alpha$ - $\beta$  transformation temperature range, while molybdenum tends to raise it. Both elements tend to promote the formation of  $\gamma$  phase, molybdenum being more potent in this respect than tungsten.

It is concluded from X-ray diffraction studies that in the Co-Cr-Mo alloys, the molybdenum is in solution in both  $\gamma$  and the two Co-rich terminal solid solutions,  $\alpha$  and  $\beta$ .

Anomalous results were obtained in  $\gamma$ -precipitation studies of alloys of nominally the same composition. It seems likely that the  $\gamma$ -precipitation characteristics of these alloys are influenced either by impurities or by prior thermal or mechanical history.

When attempts were made to correct the  $\alpha$ - $\beta$  transformation data to compensate for iron, nickel, and nitrogen present as impurities, inconsistent results were obtained; consequently, it was impossible to make the corrections. One explanation is the inaccuracy of the ternary diagrams in the regions of traces of the third element. Also, not to be overlooked are possible interactions between the trace elements and the molybdenum or tungsten present in the alloys investigated.

### Acknowledgment

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# Isothermal Transformation and Properties of a Commercial Aluminum Bronze

by A. H. Kasberg, Jr. and David J. Mack

The transformation characteristics are found to resemble a similar binary alloy. The differences are due to the alpha iron particles. While strength properties of the isothermally transformed alloys are high, ductility is low, resulting in high notch sensitivity. The elastic modulus can be varied widely and correlates with strength. Abnormal grain growth sometimes occurs.

A CONSIDERABLE amount of work has been done on the isothermal transformation of high purity aluminum bronzes using the methods pioneered by Davenport and Bain.<sup>1</sup> The first isothermal study of these alloys was made by Smith and Lindlie,<sup>2</sup> but more recently Mack<sup>3, 4</sup> and Klier and Grymko<sup>5</sup> have continued the work. In commercial aluminum bronzes, one or more elements are always added to refine the  $\beta$  grain size and to improve the mechanical properties. The effect of these elements on the isothermal transformation has not been reported in the literature.

No systematic study of the properties of isothermally transformed aluminum bronzes has apparently been reported, although adequate information is available on their properties after more conventional heat treatments. The fact that a eutectoid alloy will reject face-centered cubic  $\alpha$  during isothermal transformation at appropriate temperatures<sup>2, 3</sup> warrants investigation of the properties of such structures. Another cogent reason for determination of properties is the fact that the modulus of elasticity of the eutectoid alloy varies widely with the nature of the heat treatment.<sup>6</sup>

Preliminary experiments<sup>7</sup> indicated that a high purity eutectoid alloy would not give reproducible results in property determinations because of ex-

cessive  $\beta$  grain growth during heat treatment, a single  $\beta$  grain frequently occupying the entire cross-section of a standard test bar. For this reason a commercial aluminum bronze containing iron as a grain growth inhibitor was used.

The isothermal transformation diagram of the alloy was first determined. On this basis, the heat treatments necessary to produce representative structures were selected and the properties determined.

## Material

A commercial alloy (Ampco Grade 20) of the following composition was used: Cu, 83.68 pct; Al, 12.31 pct; Fe, 3.68 pct; Ni, 0.28 pct; and Mn, 0.03 pct. This alloy proved to be very close to the eutectoid composition and may be compared with the accepted value<sup>8</sup> of 11.8 pct Al in the binary Cu-Al system. Comparison is valid only because of the "negative replacement effect" of the iron.<sup>9</sup> Since traces of excess  $\gamma_2$  are present, the alloy is slightly hyper-eutectoid. The material was received in the form of  $\frac{3}{4}$  in. round, hot extruded bars. Specimens of approximately  $\frac{1}{8}$  in. thickness were cut from this stock and drilled to allow suspension in the salt bath.

The structure of the as-received material varied from 5 to 40 pct  $\alpha + \gamma_2^*$  in a matrix of  $\beta'$ . The amount of  $\alpha + \gamma_2$  present was dependent upon the  $\beta$  grain size of the extruded material. The coarse grained portions did not form as much  $\alpha + \gamma_2$  as did

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This paper represents part of a thesis by A. H. Kasberg, Jr. submitted in partial fulfillment of requirements for the degree of Master of Science, Metallurgical Engineering, to the Graduate Faculty of the University of Wisconsin.

\* The phases encountered in the binary Cu-Al alloy are as follows:

- $\alpha$ —Face-centered cubic copper-rich terminal solid solution.
- $\beta$ —Body-centered cubic intermediate solid solution stable above the eutectoid temperature range.
- $\beta_1$ —Ordered body-centered cubic  $\beta$ .
- $\beta'$ —Martensite structure, Al < 13 pct, nearly hexagonal close-packed.
- $\beta''$ —Appears as rosettes in  $\beta'$ . The  $\beta'$  of Smith and Lindlie.<sup>2</sup>
- $\gamma_2$ —Intermediate aluminum-rich solid solution.  $\gamma$  brass structure.
- $\gamma'$ —Martensite structure, Al > 13 pct, hexagonal close-packed.

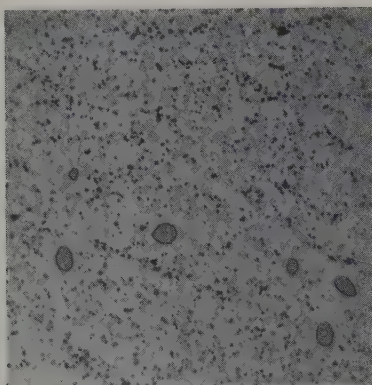


Fig. 1

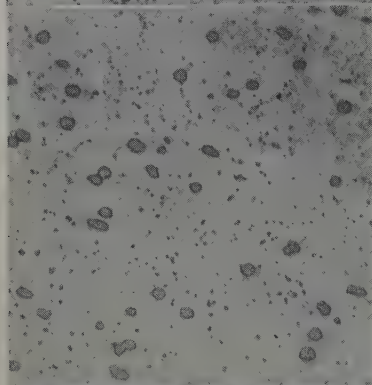


Fig. 2

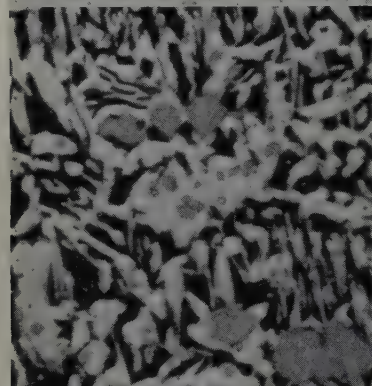


Fig. 3

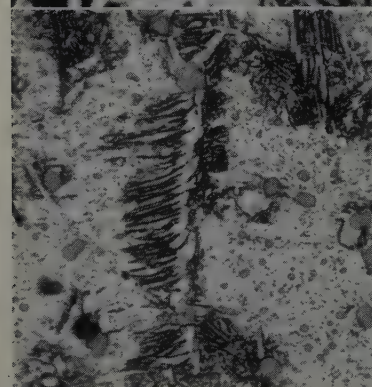


Fig. 4

Fig. 1—20 hr at 975°C, quenched 20 min at 800°C, quenched to 315°C, and held 48 hr. Iron particles in  $\beta'$ . X500.

Fig. 2—20 min at 800°C, quenched to 315°C, and held for 48 hr. Iron particles in  $\beta'$ . X500.

Fig. 3—20 min at 800°C, quenched to 550°C for 120 hr. Iron particles (medium) in an equilibrium structure of  $\alpha$  (light) and  $\gamma_2$  (dark). X2000.

Fig. 4—Transformed 16 min at 500°C.  $\alpha$  and  $\gamma_2$  in  $\beta'$ . X750.

the fine grained portions upon cooling after extrusion. The grain size was a function of the amount of work the material received in the extrusion process, the first metal to be extruded from a billet being much less drastically worked than the last metal to be extruded and hence having a coarser grain size.

Some centrifugal sand castings of this same material were also supplied by Ampco Metal, Inc., for property determination. The analyses of the extruded and cast material were nearly identical.

### Isothermal Transformation

All experimental procedures employed were those commonly used in work of this nature. The  $\frac{1}{8}$  in. wafer specimens employed for the determination of the isothermal transformation diagram were soaked 20 min at 800°C in air and quenched in the isothermal salt bath, followed by water quenching to stop the reaction. This soaking time and temperature allowed complete homogenization and no  $\beta$  grain growth was observed in specimens that contained no stress concentrators. This will be discussed in the section on abnormal grain growth. The experimental results are described in the following sections.

**Iron-rich Particles:** In view of the importance of the iron in controlling the  $\beta$  grain size and because very little material has been published concerning the behavior of the iron-rich phase, a study was made of the behavior of these particles during different thermal treatments.

These iron-rich particles have been variously defined as, "intermetallic compound,"  $\text{FeAl}_3$ , and a eutectic of  $\text{Al-FeAl}_3$ . The most accurate description of them in the literature was made by Strauss.<sup>13</sup> On the basis of much indirect evidence it was assumed that these iron-rich particles were, in actuality, b.c.c.,  $\alpha$  iron. After this hypothesis had been formulated, the authors ran across a little known paper by Yutaka<sup>14</sup> on the ternary  $\text{Cu-Al-Fe}$  system which completely confirmed the hypothesis that these "iron-rich" particles were merely  $\alpha$  iron.

Specimens were held at various temperatures in the  $\beta$  region to observe the equilibrium conditions attained between the  $\alpha$ -iron particles and the  $\beta$  matrix. Maximum solubility of the particles occurs at about 975°C. Fig. 1\*\* shows the particle distribution obtained by holding at 975°C for 20 hr, quenching in water, reheating to 800°C for 20 min and quenching in a salt bath at 315°C for a period of 48 hr, followed by a water quench. No reaction took place in the  $\beta$  matrix at the 315°C holding temperature except for the precipitation of the  $\alpha$ -iron particles. The large rounded particles indicate the amount that was not in solution at 975°C, and the small particles indicate the amount that came out of solution during the treatment at lower temperatures. The relative number of fine particles is a measure of the difference in solubility between 975° and 315°C. The arrangement of the fine particles in straight lines suggests that the particles nucleate along preferred crystallographic planes.

Fig. 2 is shown for comparison. This specimen was soaked at 800°C for 20 min and quenched in the salt bath at 315°C for 48 hr. The relative number of fine particles indicates the amount of the iron-rich phase in solution at the start of the isothermal transformations.

Fig. 3 shows the equilibrium structure attained by

\*\* Unless stated to the contrary, all specimens were etched with the ferric nitrate etch described in ref. 3.



holding for 120 hr at 550°C. The dark etching phase is  $\gamma_2$ , the light areas are  $\alpha$  and the  $\alpha$ -iron particles are an intermediate gray shade. It should be noted that the  $\alpha$ -iron particles are concentrated in the  $\alpha$  phase. At lower magnifications this causes the  $\alpha$  phase to have a mottled appearance.

The specimens held at temperatures in the  $\beta$  region were examined for grain growth. It was found that the  $\alpha$ -iron particles effectively inhibit normal grain growth for periods of 1 hr at temperatures up to 900°C.

The  $\alpha$ -iron particles apparently cause an age-hardening phenomenon when specimens are quenched from the soaking temperature of 800°C to sub-eutectoid temperatures. Fig. 12 shows a plot of hardness vs. holding time for constant temperature and is representative of the sequence of changes at all isothermal transformation temperatures. From the previously noted change in solubility of the  $\alpha$ -iron particles with temperature, it is believed that this increase in hardness, before the eutectoidal decomposition of the  $\beta$  phase occurs, is due to the precipitation of the  $\alpha$ -iron particles.

**Eutectoid Temperature Range:** The eutectoid transformation in this case is of the binary eutectoid type occurring in a three-component system. Hence, it possesses one degree of freedom and can occur over a temperature interval. The values of 576° to 592°C obtained for this temperature interval by heating curves are probably high due to thermal hysteresis. The metallographic determination gave results slightly lower than these values, but definite start and finish temperatures could not be established. Cooling curves were not taken because the alloy undercools badly. An error of 5°C due to hysteresis seems reasonable. The eutectoid temperature determined for this alloy is slightly higher than the values determined for the binary Cu-Al alloy of 556°C<sup>7</sup> to 565°C<sup>2</sup>.

**Isothermal Transformation:** An orderly pearlite reaction such as is usually found in the high purity alloys was not observed in this alloy in the extruded form, but commonly occurs in castings. Small areas sometimes develop a uniform lamellar structure, but most of the decomposition is by a rhythmical or alternate precipitation of  $\alpha$  and  $\gamma_2$ .<sup>†</sup> This results in an acicular, bainite-appearing product which may have, in fact, morphological resemblance to bainite because it develops out of concentration gradients in the  $\beta$  resulting from a pre-eutectoid precipitation. Fig. 4 illustrates this type of reaction, in which the pre-eutectoid rejection of  $\alpha$  is complete and  $\gamma_2$  is precipitating along the Widmanstätten planes giving a feathery, indistinct structure. The time-temperature-transformation diagram is shown in Fig. 5.

A few comments on the reaction at specific temperatures follow:

**545°C:** The reaction is nucleated by the iron-rich particles, the pre-eutectoid rejection of  $\gamma_2$  starting after 100 sec. The precipitation of  $\gamma_2$  apparently sets up a concentration gradient and at about 2 min a rhythmical precipitation of  $\alpha$  and  $\gamma_2$  begins. A few small areas develop a lamellar structure, but the presence of iron particles and concentration gradients interfere with its development. Fig. 6 shows the equilibrium structure of lamellar areas and coarse aggregate. The mottled appearance of the  $\alpha$  phase is due to the iron-rich particles, see Fig. 3.

<sup>†</sup> The term, "discontinuous precipitation" has been avoided because the authors believe it is commonly used when a recrystallization of the matrix occurs, and this does not happen here.

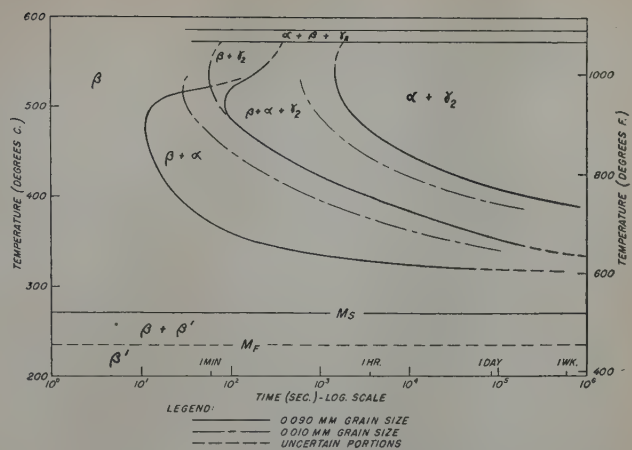


Fig. 5—Time-temperature-transformation diagram.

**500°C:** The eutectoid reaction is now preceded by the rejection of  $\alpha$  along the  $\beta$  grain boundaries and in a Widmanstätten pattern within the grains. The reaction apparently proceeds in a pattern similar to that proposed for the bainite reaction by Hultgren<sup>10</sup> and the similarity to bainite is apparent in Fig. 4. At this temperature the reaction is nucleated by both the grain boundaries and iron-rich particles.

**395°C:** The reaction is similar to that at higher temperatures but the time required is much longer and the resulting structure is finer. The nucleation and growth of the fine Widmanstätten  $\alpha$  structure takes place from both the grain boundaries and iron-rich particles. The  $\gamma_2$  areas develop in the aluminum-rich areas between the Widmanstätten plates. Fig. 7 shows the final structure attained at this temperature. It is apparent that the structure is primarily determined by the Widmanstätten rejection of  $\alpha$ .

**Effect of  $\beta$  Grain Size:** Specimens of the finest and coarsest uniform  $\beta$  grain sizes were transformed at 500°C. The fine grain specimens were obtained from the most drastically worked end of the extruded rod and had a  $\beta$  grain size of less than 0.010 mm. The coarse grained specimens were obtained by heating at 975°C for 20 hr and had a  $\beta$  grain size of about 4 mm. The start of the transformation for the fine grained specimen was found to be 30 sec at 500°C, the time required for the transformation to start in the large grained specimen being 300 sec. The maximum influence of grain size on the time required for transformation between grain size 0.010 and 4.0 mm is a factor of 10 and is similar to the effect found in Fe-C alloys.<sup>11</sup> The time-temperature-transformation curves were determined for two grain sizes, 0.010 and 0.090 mm. Both curves are shown for comparison in Fig. 5.

**Martensite Reaction:** It was apparent from the thermal characteristics of the martensite reaction in this aluminum bronze that it is endothermic while the martensite reaction in steel is exothermic. The slope of the time-temperature cooling curve for the aluminum bronze is the same before and after the martensite reaction.

The value obtained for the  $M_s$  temperature was 270°C as indicated in Fig. 5. This compares with an  $M_s$  temperature of 370°C for the high purity binary alloy. Examination of the  $\beta'$  structure by polarized light on longitudinal sections cut from the extruded bars showed some preferential orientation of the  $\beta$  phase.

**Abnormal Grain Growth:** Abnormal grain growth was encountered in this study of the isothermal





Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 6—Transformed 3 hr at 545°C. Transformation is complete. A rhythmical precipitation of  $\alpha$  and  $\gamma_2$  with a small area of pearlite is shown. X750.

Fig. 7—Transformed 48 hr at 395°C. Equilibrium structure of  $\alpha$  and  $\gamma_2$ . X750.

Fig. 8—Transformed 10 sec at 450°C. Grains growing from drilled hole. 20 pct  $\text{HNO}_3$  etch. X8.

Fig. 9—Transformed 20 sec at 450°C. Grain growth in the neighborhood of seams resulting from the extrusion process. 20 pct  $\text{HNO}_3$  etch. X8.

Fig. 10—Transformed 10 sec at 315°C. Martensite structure visible within the large grains. 20 pct  $\text{HNO}_3$  etch. X3.3.

transformation of a commercial aluminum-bronze. Large grains developed during isothermal transformation at temperatures of 450°C or lower. The grain growth occurred in the retained  $\beta$  phase before the martensite reaction started at a temperature of 270°C. The grain growth was apparently nucleated by mechanically induced interruptions in the normally symmetrical stress pattern resulting from thermal contraction during quenching in the isothermal bath.

Investigation of this phenomenon showed that extruded specimens transformed at temperatures higher than 450°C showed no evidence of grain growth, since quenching stresses were not large enough. Specimens transformed at 450°C showed that grain growth had started at mechanical stress concentrators, Figs. 8 and 9. At this temperature the isothermal grain boundary reaction started in about 10 sec, which stopped the grain growth. Specimens that were quenched to lower temperatures or directly to room temperature showed extensive grain growth, Fig. 10. The structure within the large grains exhibits martensite needles that extend the full width of the grain, indicating that the grain growth was complete before the martensite start temperature of 270°C was reached.

Only specimens with eccentrically positioned stress concentrators showed abnormal grain growth. In specimens with drilled holes at or near the center there was no abnormal grain growth even when a dull drill was used. In this case normal recrystallization occurred in the cold-worked area around the hole, but this grain growth was not abnormal. The sand-cast specimens provided an excellent illustration of the effect of the nonuniform stress pattern on abnormal  $\beta$  grain growth. They were heat treated as-cast in the irregularly shaped bars and without exception showed very large  $\beta$  grains; the extruded specimens were heat treated as uniform cylinders and showed no abnormal grain growth unless internal seams were present to provide the stress concentration. The sand-cast specimens showed abnormal grain growth at all isothermal temperatures.

*Discussion:* The isothermal transformation of this alloy was essentially the same as that encountered in binary alloys.<sup>2, 3, 5</sup> The primary differences are: the raising of the eutectoid temperature and its expansion into a three-phase field; the lowering of the martensite start temperature; and the effect of the iron-rich particles in nucleating the decomposition and interfering with the development of a uniform pearlitic structure.

The coarsest structures were obtained at the highest transformation temperature, and the structures became progressively finer as the transformation temperature was lowered. This was to be expected due to the decrease in diffusion rates with a decrease in temperature.



The  $\beta''$  rosettes observed by Smith and Lindlie<sup>2</sup> and Mack<sup>3</sup> in high purity eutectoid Cu-Al alloys were not observed in this alloy.

The presence of an ordering reaction or the presence of  $\gamma'$  in the partially transformed specimens was not determined since an X-ray diffraction analysis was not made.

Properties

**Experimental Procedure:** The extruded rod was cut to pieces 5½ in. in length, every third specimen being 6½ in., thus allowing a 1 in. section for removal for metallographic examination and hardness determination. The specimens were heat treated in groups of three. They were soaked at 800°C for 30 min in air and then quenched in the isothermal salt bath held at various subeutectoid temperatures. Specimens that had completely transformed in the salt bath were then air-cooled to prevent cracking, since structures composed of  $\alpha$  and  $\gamma_2$  are very brittle. Other specimens held for intermediate time intervals, thus allowing only partial transformation, were quenched in cold water to arrest the transformation.

A dynamic modulus of elasticity was then determined on each cylindrical heat-treated specimen using it as a "free-free" beam, vibrated at its natural frequency. This dynamic testing machine was designed and built by W. T. Thomson, of the Mechanics Department, University of Wisconsin.

After dynamic modulus determination the cylindrical specimens were machined to standard 0.505 in. tensile bars and pulled in a universal testing machine. The static modulus of elasticity was obtained by plotting the stress-strain curve and taking

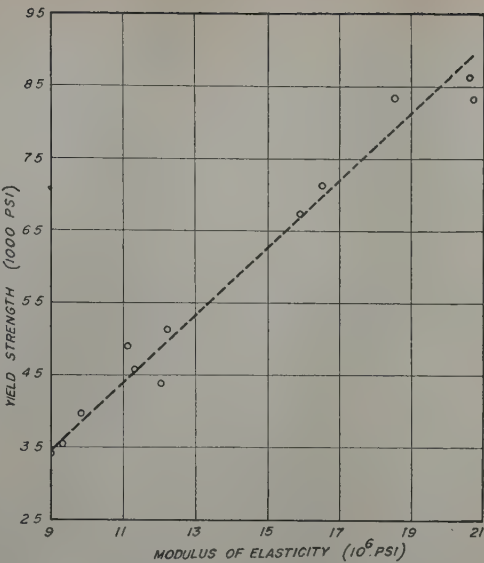


Fig. 11—Yield strength as a function of the modulus of elasticity of Ampco 20.

the slope of a tangent drawn at one third the yield strength (based on 0.5 pct elongation). This point was chosen since it would approximate the allowable working stress in this alloy in service. The results of the property determinations are shown in Table I.

**Discussion:** The stress-strain curves for these aluminum bronze structures are continuous curves, but at higher values of hardness and strength the lower portion of the curve approaches a straight

Table I. The Properties of an Isothermally Transformed Commercial Aluminum Bronze (Ampco 20)

| Specimen No.                    | Iso-thermal Trans-formation Temperature, °C | Time at Temperature | Brinell Hardness No.           | Ultimate Tensile Strength, 1000 psi | Yield Strength 0.5 Pct Elong., 1000 psi | Elongation in 2 In., Pct | Reduction in Area, Pct | Dynamic Modulus of Elasticity, 10 <sup>6</sup> psi | Static Modulus of Elasticity (at 1/3 Yield Strength), 10 <sup>6</sup> psi | Microstructure ( $\alpha$ -Iron Particles Are Always Present in Addition to the Phases Below.) |
|---------------------------------|---------------------------------------------|---------------------|--------------------------------|-------------------------------------|-----------------------------------------|--------------------------|------------------------|----------------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| PART A—Cut from Extruded Bars.* |                                             |                     |                                |                                     |                                         |                          |                        |                                                    |                                                                           |                                                                                                |
| 1A                              | 545±5                                       | 8 min               | 217                            | 111                                 | 43                                      | 4.2                      | 4.2                    | 13.3                                               | 11.8                                                                      | Pre-eutectoid $\gamma_2$ in $\beta'$                                                           |
| 2A                              | 545±5                                       | 28 min              | 277                            | 107                                 | 81                                      | 0                        | 0                      | 20.4                                               | 20.4                                                                      | $\alpha$ and $\gamma_2$                                                                        |
| 3A                              | 545±5                                       | 2 min               | 285                            | 118                                 | 83                                      | 0                        | 0                      | 20.5                                               | 20.7                                                                      | $\alpha$ and $\gamma_2$ (equilibrium)                                                          |
| 1B                              | 500±5                                       | 1 min               | 248                            | 118                                 | 44                                      | 4.7                      | 3.8                    | 13.0                                               | 12.1                                                                      | Pre-eutectoid $\alpha$ in $\beta'$                                                             |
| 2B                              | 500±5                                       | 5 min               | 277                            | 111                                 | 62                                      | 1.7                      | 1.7                    | 16.0                                               | 15.3                                                                      | 10 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                     |
| 3B                              | 500±5                                       | 8 min               | 302                            | 123                                 | 83                                      | 0                        | 0                      | 19.7                                               | 18.6                                                                      | 70 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                     |
| 1C                              | 455±5                                       | 8 min               | 248                            | 109                                 | 57                                      | 2.5                      | 2.7                    | 14.7                                               | 13.9                                                                      | 5 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                      |
| 2C                              | 455±5                                       | 20 min              | 277                            | 118                                 | 67                                      | 1.2                      | 1.5                    | 16.8                                               | 15.9                                                                      | 20 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                     |
| 3C                              | 455±5                                       | 40 min              | 293                            | 102                                 | 86                                      | 0                        | 0                      | 20.0                                               | 20.6                                                                      | 98 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                     |
| 4C                              | 455±5                                       | 1 hr                | Specimens cracked in quenching |                                     |                                         |                          |                        |                                                    |                                                                           |                                                                                                |
| 5C                              | 455±5                                       | 2 hr                | 293                            | Specimens cracked in quenching      |                                         |                          |                        |                                                    |                                                                           |                                                                                                |
| 1D                              | 395±5                                       | 2 min               | 241                            | 107                                 | 46                                      | 4.7                      | 4.8                    | 13.2                                               | 11.3                                                                      | $\alpha$ and $\gamma_2$ (equilibrium)                                                          |
| 2D                              | 395±5                                       | 11 min              | 241                            | 115                                 | 48                                      | 3.5                      | 3.2                    | 13.1                                               | 11.2                                                                      | Pre-eutectoid $\alpha$ in $\beta'$                                                             |
| 3D                              | 395±5                                       | 1 hr                | 255                            | 119                                 | 51                                      | 2.5                      | 3.3                    | 13.4                                               | 12.2                                                                      | Pre-eutectoid $\alpha$ in $\beta'$                                                             |
| 4D                              | 395±5                                       | 6 hr                | 285                            | 118                                 | 71                                      | 0.8                      | 0.8                    | 16.5                                               | 16.5                                                                      | 1 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                      |
| 5D                              | 395±5                                       | 14 hr               | 313                            | 131                                 | 92                                      | 0                        | 0                      | 20.4                                               | 21.5                                                                      | 15 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                     |
| 6D                              | 395±5                                       | 48 hr               | 317                            | 131                                 | 94                                      | 0                        | 0                      | 20.8                                               | 21.6                                                                      | $\alpha$ and $\gamma_2$                                                                        |
| 1E                              | 350±5                                       | 4 min               | 241                            | 106                                 | 36                                      | 4.7                      | 3.5                    | 11.4                                               | 9.3                                                                       | $\alpha$ and $\gamma_2$ (equilibrium)                                                          |
| 2E                              | 350±5                                       | 4 hr                | 255                            | 110                                 | 40                                      | 2.3                      | 3.0                    | 11.5                                               | 9.8                                                                       | Pre-eutectoid $\alpha$ in $\beta'$                                                             |
| 3E                              | 350±5                                       | 42 hr               | 272                            | 116                                 | 48                                      | 1.6                      | 2.0                    | 12.4                                               | 11.1                                                                      | Pre-eutectoid $\alpha$ in $\beta'$                                                             |
| Q                               | Quenched from 800°C                         |                     | 217                            | 112                                 | 44                                      | 4.5                      | 5.3                    | 13.0                                               | 12.0                                                                      | 2 pct $\alpha$ and $\gamma_2$ in $\beta'$                                                      |

PART B—Centrifugal Sand Castings.\*\*

| Sand-cast | Average quoted properties in "as-cast" condition <sup>1a</sup> |       | 207 | 85 | 40 | 4.0 | 3.5 | 12.0                                            | Pre-eutectoid $\alpha$ and lamellar ( $\alpha + \gamma_2$ ) eutectoid in $\beta'$ |
|-----------|----------------------------------------------------------------|-------|-----|----|----|-----|-----|-------------------------------------------------|-----------------------------------------------------------------------------------|
| 2784-1A   | 545±5                                                          | 8 min | 217 | 59 | 36 | 1.0 | 2.7 | 1 specimen only, others broke in machining      | Pre-eutectoid $\gamma_2$ in $\beta'$                                              |
| 2784-1C   | 455±5                                                          | 8 min | 212 | 50 | 34 | 1.5 | 1.4 | 2 specimens                                     | Pre-eutectoid $\alpha$ in $\beta'$ traces of lamellar eutectoid                   |
| 2784-5D   | 395±5                                                          | 14 hr |     | 76 | 55 | 0.5 | 0   | 1 specimen only, others broke in Brinell tester | Pre-eutectoid $\alpha$ and 35 pct lamellar eutectoid in $\beta'$                  |
| 2784-2E   | 350±5                                                          | 4 hr  |     |    |    |     |     | All bars broke during machining                 | Pre-eutectoid $\alpha$ in $\beta'$                                                |

\* All property values are an average of three specimens.

\*\* All specimens showed abnormal grain growth.

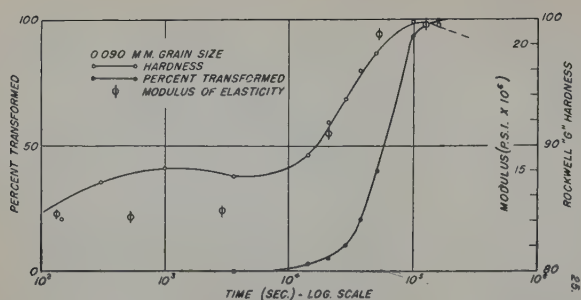


Fig. 12—Percentage transformation, hardness, and modulus of elasticity vs. holding time at 400°C.

line. When the yield strength is chosen at 0.5 pct elongation, the yield strength is a function of the modulus of elasticity as shown in Fig. 11.

The physical properties are plotted as a function of structure in Figs. 12 and 13 for an isothermal transformation temperature of 400°C. At 100 sec the pre-eutectoid rejection of  $\alpha$  has started and an apparent age-hardening reaction due to the iron phase present begins. The hardness and tensile strength increase but the elastic properties remain fairly constant. At about 5000 sec the eutectoid reaction of  $\beta \rightarrow \alpha + \gamma_2$  begins and hardness, strength and elastic properties increase and approach a maximum when the reaction is about 60 pct complete. At this point the  $\alpha + \gamma_2$  aggregate apparently forms a continuous path through the structure. The plastic properties (i.e., elongation and reduction in area) decrease with a further increase in holding time and drop to zero shortly after the eutectoid reaction starts.

The structures obtained at the lower transformation temperatures are finer than the high temperature structures and give a better combination of properties. The high temperature structures appear to be very sensitive to notches and all such specimens failed in tension at the gage marks. Some of the specimens treated at lower temperatures also failed at gage marks. The result of this notch sensitivity is a wide spread in the experimental results.

The agreement between values of the modulus by the dynamic method and the static method is very good and most discrepancies can be correlated to the shape of the stress-strain curve.

Because of the bad effect of the abnormal grain growth on properties and the fact that this abnormal grain growth will occur whenever a change in section size exists, the adaptation of isothermal transformation to commercial heat treatment of this particular aluminum bronze seems out of the question. Any improvement in properties that might be obtained by isothermal treatment would be masked or endangered by the omnipresent possibility of abnormal grain growth.

### Summary

1—The change in solubility of the  $\alpha$ -iron particles with temperature has been shown to cause an age-hardening effect during subsequent isothermal holding. The iron particles are effective in preventing  $\beta$  grain growth for periods up to 1 hr at 900°C.

2—The eutectoid transformation occurs over a temperature range (576° to 592°C) showing this aluminum bronze behaves as a true ternary alloy.

3—The isothermal transformation characteristics do not differ much from those of the binary Cu-Al alloy. Lamellar pearlite does not form readily in the extruded alloy but is common in the cast material. The major portion of the decomposition of  $\beta$  is by

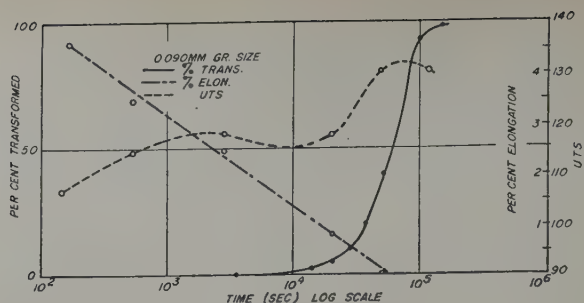


Fig. 13—Percentage transformation, percentage elongation in 2 in., and ultimate tensile strength vs. holding time at 400°C.

rhythmic or alternate precipitation of  $\alpha$  and  $\gamma_2$ . No rosettes of  $\beta''$  were observed.

4—The effect of variations in  $\beta$  grain size on the transformation times is the same as commonly observed for other alloys, fine grains resulting in more rapid transformation.

5—This alloy has a most unusual tendency for abnormal  $\beta$  grain growth in the isothermal bath. The tendency is associated with nonuniform stresses set up in the specimen during the quench into the isothermal bath.

6—While high ultimate tensile and yield strengths can be obtained by isothermal transformation, these high strengths are accompanied by low elongation and reduction in area values which lead to very high notch sensitivity.

7—The modulus of elasticity can be varied over a relatively enormous range by suitable isothermal transformation.

8—The commercial use of isothermal heat treatments for this particular alloy does not seem worthwhile because of the low ductility and susceptibility to abnormal  $\beta$  grain growth.

### Acknowledgments

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# Creep and Stress Rupture Behavior of Aluminum

## As a Function of Purity

by Italo S. Servi and Nicholas J. Grant

**Extensive data of minimum creep rates and rupture times for high purity and commercial aluminum confirm the existence of a transition range from the low temperature-type to the high temperature-type behavior. The data are analyzed in line with the suggested theories of deformation of metals.**

CONSIDERABLY more work has been done on the rupture and creep behavior of commercial alloys than on the less complex, high purity metals. As a result, certain fundamental behaviors are overlooked. One of the lesser known variables affecting the high temperature behavior of metals is the impurity content (or alloy content). Impurities are known to affect strongly the recrystallization temperature, electrical resistivity, and other properties of metals, but the effect on creep and other high temperature mechanical properties has been determined for very few materials.

In view of these facts aluminum appears to be a fairly ideal metal, since it is available in a wide range of purity contents from 99.995+ down through the 2S (99.0 + Al) and 3S (1.2 Mn) grades in small steps. It is highly resistant to oxidation and other surface instabilities, leaving recrystallization and grain growth as virtually the only instabilities. Control of grain size is also well standardized.

Limited data on the creep of aluminum have been obtained by Dushman et al.<sup>1</sup> for high purity aluminum; by Sherby<sup>2</sup> on 2S aluminum of variable grain size; and by Dorn and Tietz<sup>3</sup> on cold-worked 3S aluminum.

### Experimental Procedure

The apparatus consisted of a constant stress, creep testing unit similar to the type described by Hopkin.<sup>4</sup> The specimens were held at temperature for 30 min before loading. The loading time was less than 2 min. Factors affecting the accuracy of the data were: 1—the temperature gradient and control,  $\pm 3^\circ\text{F}$ ; 2—the stress determinations,  $\pm 1.5$  pct; and 3—elongation measurements (1 in. gage),  $\pm 0.001$

in. Three grades of aluminum were tested: 1—high purity (99.995 pct Al), 2—2S (99.3 pct Al), and 3—3S (98.2 pct Al).

The spectrographic analyses of these materials are reported in Table I. The specimens were annealed then electropolished in a perchloric-acetic mixture before testing. Data on heat treatments and grain size obtained appear in Table II.

The entire creep curve was determined for almost all of the tests. A few tests were interrupted after the beginning of the third stage of creep, and in these cases the rupture time was estimated.

### Experimental Results

Constant stress creep-rupture testing gives a much longer, more accurately measurable second stage of creep than constant load testing. This behavior is in agreement with the results obtained by Andrade<sup>5</sup> for lead (see Fig. 1). If the test is run to completion, the third stage of creep appears as soon as stress intensification occurs. In the case of specimens which fail in a ductile manner, the stress intensification begins when the sample starts "necking". This differs from the "high temperature brittle" specimens in which the stress intensification is caused by intercrystalline cracking. These specimens

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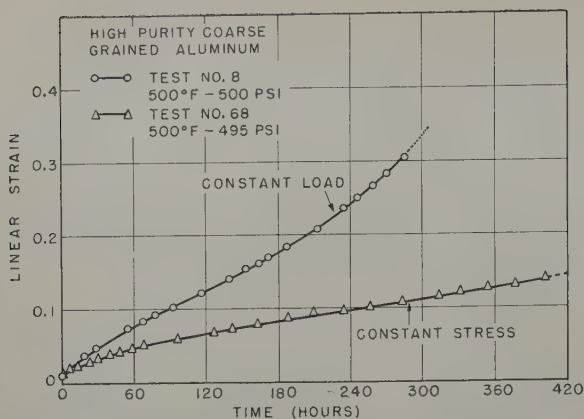


Fig. 1—Typical creep curves for high purity aluminum obtained from tests made at constant load and at constant stress.

fail by parting along the grain boundaries. Fig. 2 shows typical creep curves for two samples: a high purity aluminum sample which failed in a ductile manner, and a 3S aluminum sample which failed in a brittle manner. In case intercrystalline cracking occurs, as for the 3S sample mentioned above, there is no way of completing the test without entering third stage creep because of the inability to measure the area of sound metal in the cross-section.

All the data are expressed in terms of linear strains and linear strain rates. It was found that the use of true strain and true strain rate did not change the fundamental results and conclusions, and merely shifted the log-log curves of the following figures relative to one another.

The minimum creep rates have been calculated by determining the slope of the straight portion of the creep curves, as indicated by the broken lines of the sample creep curves of Fig. 2.

**Stress Dependence of Minimum Creep Rate:** Fig. 3 shows a plot of the stress vs. the log of the minimum creep rate for high purity aluminum. The data of Dushman et al.<sup>1</sup> are included (dotted lines) for comparison.

Dushman et al.<sup>1</sup> and Kauzmann<sup>6</sup> in applying the Eyring theory of activated complex<sup>7</sup> to the creep of metals predicted that a straight line should be ob-

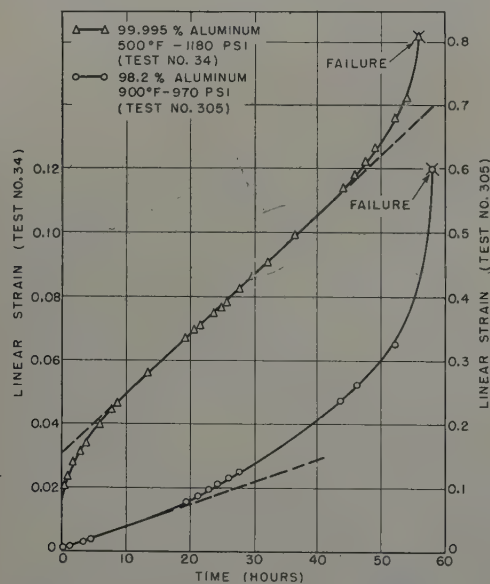


Fig. 2—Typical creep curves for a specimen which failed in a ductile manner (test No. 34) and a specimen which failed in a brittle manner (test No. 305).

Note the different strain scales.

tained when the stress is plotted vs. the logarithm of the creep rate. This straight line corresponds to an approximation of the hyperbolic sine law. It was shown previously by Grant and Bucklin<sup>8</sup> that the predicted straight line semilog plots of stress vs. minimum creep rate do not exist over wide ranges of creep rate values. However, since the work was done on a very complex, high temperature-type alloy, while Dushman et al. used high purity aluminum and other pure metals, it seemed quite logical to try to confirm Grant and Bucklin's observations by using aluminum of comparable purity. If there is a measurable effect of impurity content on the viscous behavior of metals, this should also be apparent in the creep tests.

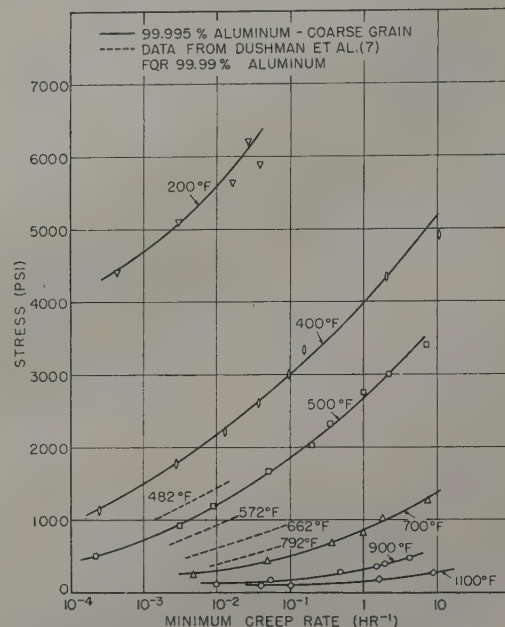


Fig. 3—Semilog plot of stress vs. minimum creep rate for high purity, coarse grained aluminum.

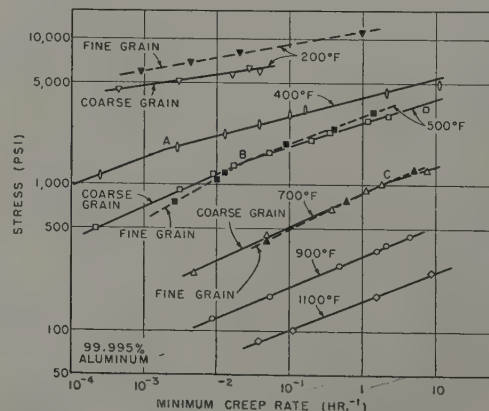


Fig. 4—Log-log plot of stress vs. minimum creep rate for high purity, coarse grained and fine grained aluminum.

Fig. 3 for high purity aluminum does lead to the same conclusions as those obtained by Grant and Bucklin on alloy S-590. Smooth curves best represent the experimental points. The straight lines of Dushman et al. simply serve as an approximation over a limited range of creep rate values. While straight line segments would easily be selected, there is no good guide for such selection. A change in slope of the curve, interpreted in terms of Eyring's theory, would indicate an increase in the size of the "units of flow" occurring when the material assumes a more viscous behavior.



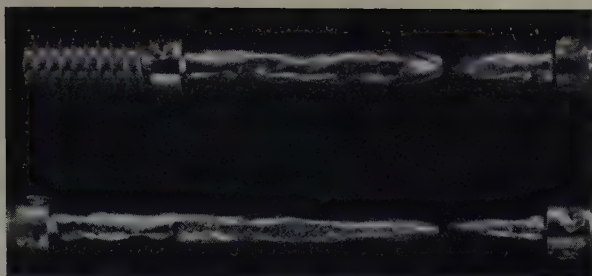


Fig. 5—High purity, coarse grained aluminum. Upper: Low temperature test, 400°F. Rupture time, 0.07 hr. Lower: High temperature test, 900°F. Rupture time, 0.33 hr.

Eyring's theory may possibly be applicable to the flow of metals at much slower strain rates, or much higher temperatures, than the strain rates and temperatures investigated. Under these conditions the metal may, in fact, be deforming by a purely viscous mechanism.

The log-log plot of stress vs. minimum creep rate for high purity aluminum is presented in Fig. 4. This plot shows that straight line segments are ob-

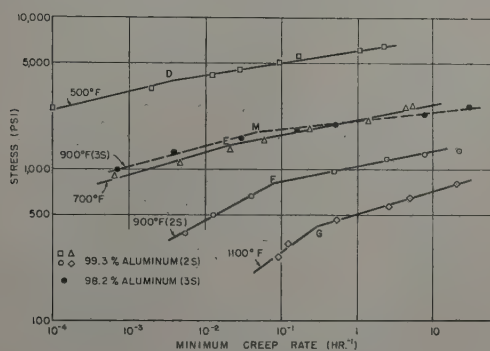


Fig. 6—Log-log plot of stress vs. minimum creep rate for 2S and 3S aluminum.

served at all temperatures. However, a change in slope is evident in the 500°F curve, and less clearly in the curves for 400° and 700°F.

These "breaks" locate three transition points, A, B, and C, which were not readily apparent in Fig. 3. Metallographic examination revealed that if the testing conditions are above the line A-B-C, the grain boundaries are stronger than the grains. Under these conditions, the grain boundaries do not make any contribution to the deformation of the



Fig. 7—Change in type of fracture of 2S aluminum as conditions of testing change.

Testing temperature, 900°F. Rupture times (left to right): 0.02 hr (low temperature); 18.4 hr (transition); 41.5 hr, 81.5 hr (high temperature).



Fig. 8—Change in type of fracture of 3S aluminum as conditions of testing change.

Testing temperature, 900°F. Rupture times (left to right): 0.023 hr (low temperature); 0.93 hr (low temperature, approaching the transition); 4.1 hr (high temperature, near transition); 58 hr (high temperature).

sample and only hinder the deformation of the grains (low temperature-type behavior). Below the line A-B-C the grain boundaries are weaker than the grains and contribute to the deformation of the specimen, and do not restrict the deformation of the grains (high temperature-type behavior).

The transition line A-B-C is the line of "equi-cohesion" for grains and grain boundaries. This conclusion is supported by the fact that the fine grained material (dotted lines of Fig. 4) is stronger

Table I. Spectrographic Analysis of the Impurities Contained in Three Grades of Aluminum Used for Creep and Stress Rupture Testing\*

| Type of Aluminum | Impurities, Pct |       |       |      |        |      |      |      |               | Na, Ca |
|------------------|-----------------|-------|-------|------|--------|------|------|------|---------------|--------|
|                  | Cu              | Fe    | Si    | Mn   | Mg     | Zn   | Cr   | Ti   | Pb, Ni, Bi, B |        |
| High purity      | 0.0017          | 0.002 | 0.001 |      | 0.0002 |      |      |      |               | 0.0006 |
| 2S               | 0.11            | 0.47  | 0.12  | 0.01 | 0.00   | 0.01 | 0.00 | 0.03 | 0.00          |        |
|                  | 0.10            | 0.46  | 0.12  | 0.01 | 0.00   | 0.01 | 0.00 | 0.03 | 0.00          |        |
| 3S               | 0.09            | 0.37  | 0.16  | 1.15 | 0.00   | 0.01 | 0.01 | 0.01 | 0.00          |        |
|                  | 0.09            | 0.36  | 0.16  | 1.15 | 0.00   | 0.01 | 0.01 | 0.01 | 0.00          |        |

\* The three grades of aluminum and their spectrographical analyses were furnished by the Aluminum Co. of America.

Table II. Data on Aluminum Used in Test Program

| Material                     | "As-Received" |        |                       | Heat Treatment  |          | After Heat Treatment Grain Size, mm |                                     |
|------------------------------|---------------|--------|-----------------------|-----------------|----------|-------------------------------------|-------------------------------------|
|                              | Shape         | Temper | Grain Size            | Temperature, °F | Time, Hr | Cross-Section                       | Longitudinal Section                |
| High purity, fine grained*   | 3/8 in. rod   |        | 1000 grains per cu mm | 650             | 0.5      | 0.05                                | 0.05                                |
| High purity, coarse grained* | 3/8 in. rod   |        | 1000 grains per cu mm | 650             | 0.5      | 1 to 3                              | 1 to 3                              |
|                              |               |        |                       | 1000            | 0.5      | (20 to 30 grains per cross-section) | (20 to 30 grains per cross-section) |
| 2S                           | 5/16 in. rod  | H-18   |                       | 1000            | 3        | 0.02 to 0.03                        | 0.02 to 0.03                        |
| 3S                           | 3/8 in. rod   | F      |                       | 1000            | 3        | 0.05 to 0.1                         | 0.1 to 0.4                          |

\* The terms "fine grained" and "coarse grained" refer to the grain size of the sample before testing.

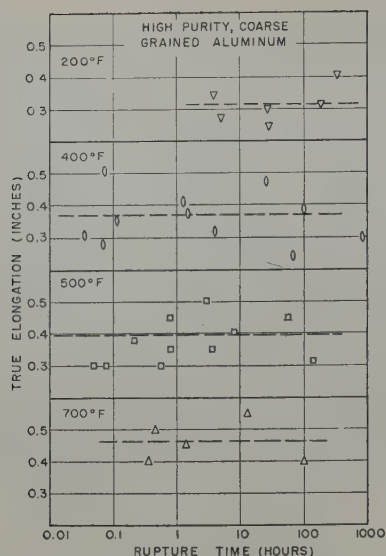


Fig. 9—True elongation vs. logarithm of rupture time for high purity, coarse grained aluminum.

than the coarse grained material (solid lines of Fig. 4) in the low temperature region, while the reverse is true in the high temperature region.

It is interesting to note that the very marked grain growth which occurred in tests made at 900° and 1100°F shows up as an instability. This is evidenced by the fact that the slopes of the 900° and 1100°F curves are smaller than the slope of the 700°F curve. However, the same instability is not detectable by inspecting the curves of Fig. 3 (semilog plot).

The fractures of all the specimens were typically ductile, but the shape of the rupture zone changed slightly with the conditions of testing, see Fig. 5.

Fig. 6 shows the log-log plot of stress vs. minimum creep rate for 2S and for 3S aluminum. Straight line segments are obtained at all temperatures, with changes in slope shown at the transition points D, E, F, and G for 2S aluminum and at M for 3S aluminum. The curve at 700°F shows a smaller change in slope than expected, with some evidence that the longest time tests are showing improved resistance to creep. A check of the hardness showed, in fact, that for rupture times greater than 20 hr, there was a hardness increase of about 3 Brinell points.<sup>8</sup>

The ductile nature of the fractures above a line through points D, E, F, and G and above M, and the

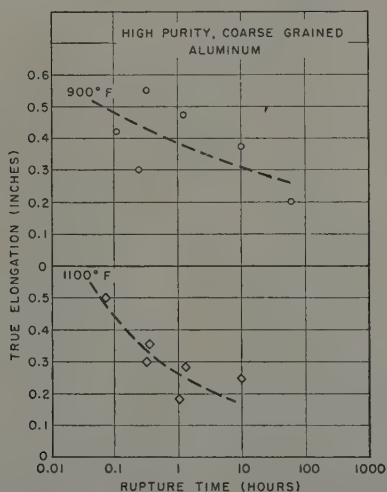


Fig. 10—True elongation vs. logarithm of rupture time for high purity, coarse grained aluminum.

brittle intercrystalline fracture below these points is shown in Fig. 7 for 2S aluminum and in Fig. 8 for 3S aluminum.

Metallographic observations revealed more definite evidence of grain boundary flow and grain boundary cracking in the 2S and 3S specimens tested under high temperature conditions. These observations confirm the conclusion that the transitions at D, E, F, G, and M correspond to equicohesion for the grains and grain boundaries.

**Ductility:** A study of the ductility as a function of purity and conditions of testing was made by plotting the true elongation vs. the logarithm of the rupture time, Figs. 9, 10, and 11. The "true elongation" was defined by Grant and Bucklin<sup>9</sup> as the elongation occurring up to the incidence of third stage creep.

Fig. 9 shows that the true elongation data for high purity aluminum tested at 200°, 400°, 500°, and 700°F are scattered around average values. The average value of the true elongation increases as the temperature increases. Fig. 10 indicates that at 900°

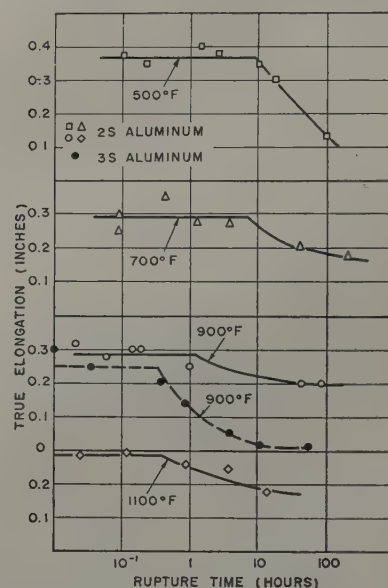


Fig. 11—True elongation vs. logarithm of rupture time for 2S and 3S aluminum.

and 1100°F the true elongation of high purity aluminum decreases as the rupture time increases. At these temperatures marked grain growth occurred during testing.

Fig. 11 demonstrates that the true elongation of 2S and 3S aluminum markedly drops at the transition from low temperature-type to high temperature-type deformation. The decrease in true elongation is much sharper for 3S than for 2S. For both materials the decrease in true elongation corresponds to the incidence of intercrystalline cracking.

**Stress Dependence of Rupture Times:** Results

Table III. Calculated and Experimental Transition Temperatures for High Purity, Coarse Grained Aluminum

| Testing Temperature, °F | Transition Stress, Psi | Transition Creep Rate, Hr <sup>-1</sup> | Transition Temperature (T <sub>c</sub> ) |                 |
|-------------------------|------------------------|-----------------------------------------|------------------------------------------|-----------------|
|                         |                        |                                         | Calculated °K                            | Experimental °K |
| 400                     | 1950                   | 0.001                                   | 460                                      | 477             |
| 500                     | 1400                   | 0.03                                    | 510                                      | 533             |
| 700                     | 1000                   | 1.7                                     | 585                                      | 644             |



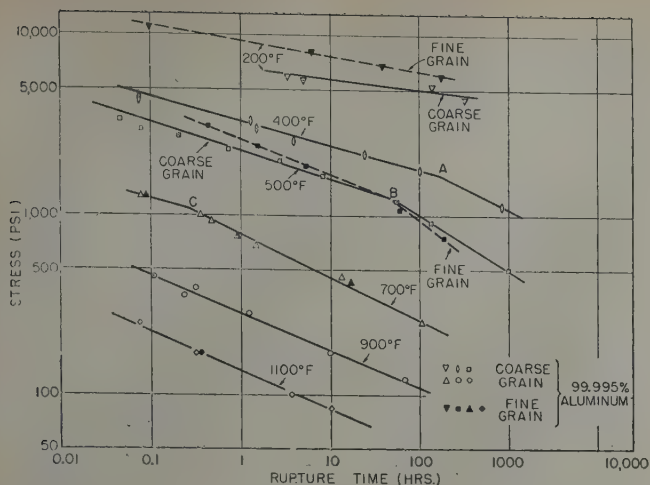


Fig. 12—Log-log plot of stress vs. rupture time for high purity aluminum.

similar to those shown in log-log plots of stress vs. minimum creep rate (Figs. 4 and 6) were obtained when the logarithm of the rupture time was plotted vs. the logarithm of the stress. Fig. 12 (high purity aluminum) and Fig. 13 (2S and 3S aluminum) show that a series of "breaks" are found for each material investigated. A continuous straight line could be drawn through the 1100°F points of Fig. 13. The curve drawn in Fig. 13 for this temperature is based on the uncertainty of the last point, which was affected by excessive secondary recrystallization.

The log-log plots "stress vs. minimum creep rate" and "stress vs. rupture time" are almost mirror images. This behavior can be explained by assuming that the minimum creep rate is inversely proportional to the rupture time:

$$\text{M.C.R.} = \frac{E_0}{\text{R.T.}} \quad [1]$$

where  $E_0$  is a constant.

As a first approximation all the test results for high purity and 2S aluminum follow eq 1. In fact, a log-log plot of minimum creep rate vs. rupture time gives a band slope  $-1$ , with a reasonably limited scatter (see Figs. 14 and 15). The high temperature points obtained for 3S aluminum deviate from eq 1. The different behavior of these specimens may be ascribed to their comparatively low ductility.

**Transition Stresses and Transition Strain Rates:** The average values of the transition stresses and of the transition strain rates, as determined from the "breaks" in the isothermal lines of Fig. 4 (points A, B, C) and Fig. 6, (points D, E, F, G, M) and from

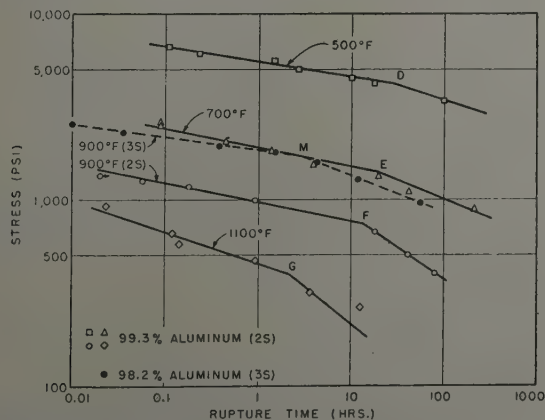


Fig. 13—Log-log plot of stress vs. rupture time for 2S and 3S aluminum.

the results of metallographic examinations, are plotted vs. the temperature in the semilog plots of Figs. 16 and 17, respectively. The results indicate that: 1—Impurities raise the transition stress for a given temperature. 2—Impurities lower the transition strain rate for a given temperature. 3—The transition stress and strain rate have definite values at temperatures close to the melting point. 4—Below a certain critical temperature, no transition will be observed within a reasonable testing time.

The results of Fig. 16 are in good agreement with the results obtained by Grant and Bucklin<sup>9</sup> for cobalt-base alloys, however, the present experimental results were obtained close to the melting point, whereas considerable extrapolation had been necessary in working with the complex S-590 alloy because creep rupture tests had to be limited to 1800°F (melting point 2450°F). An attempt has been

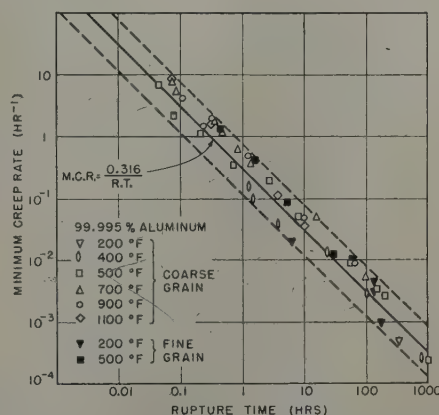


Fig. 14—Log-log plot of minimum creep rate vs. rupture time for high purity aluminum.

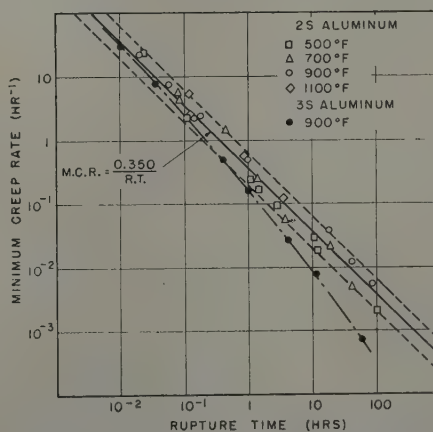


Fig. 15—Log-log plot of minimum creep rate vs. rupture time for 2S and 3S aluminum.

made to compare the experimental results reported above on the transition temperature with the Mott theory of grain boundary slip.<sup>10</sup> According to Mott, viscous flow cannot occur along the grain boundaries below a critical temperature  $T_c$ , which is defined by the equation:

$$T_c = \frac{Q}{R \ln \left( \frac{b \sigma}{x \dot{\epsilon}} \right)} \quad [2]$$

where  $Q$ ,  $b$  are constants associated with the viscous flow at the grain boundaries;  $\sigma$  is the applied stress;  $x$ , the linear grain size;  $\dot{\epsilon}$ , the creep rate; and  $R$ , the gas constant.

Based on Kê's work<sup>11</sup> with 99.991 pct Al, Mott

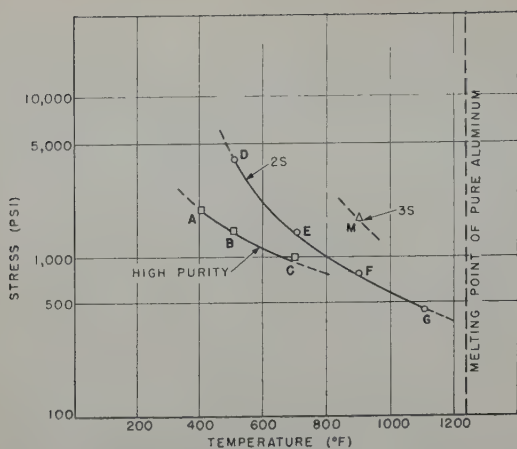


Fig. 16—Logarithm of transition stress vs. temperature for high purity, coarse grained 2S and 3S aluminum.

calculated the theoretical critical temperature for aluminum and obtained a value of 410°K (277°F) for "normal" creep testing conditions.

The theoretical critical temperatures corresponding to the conditions of testing used in the present investigation have been calculated in a similar way. The results are presented in Table III.

Eq 2 can be re-written as follows:

$$\text{Log } \frac{\sigma}{\dot{\epsilon}} = A + \frac{B}{T_c} \quad [3]$$

where  $\sigma$  is the transition stress, and  $\dot{\epsilon}$  is the transition strain rate for the temperature  $T_c$ .  $A$  and  $B$  are constants proper of the material.  $\frac{\sigma}{\dot{\epsilon}}$  is a measure of the grain boundary viscosity.

Utilizing Mott's values for  $Q$  and  $b$  from eq 2 and expressing the stress  $\sigma$  in psi and the creep rate  $\dot{\epsilon}$  in  $\text{hr}^{-1}$ , the constants  $A$  and  $B$  for aluminum are:  $A = -10.4$  and  $B = 7680$ .

The logarithm of  $\frac{\sigma}{\dot{\epsilon}}$  was plotted vs. the reciprocal of the absolute temperature in Fig. 18. Straight lines were obtained for high purity and for 2S aluminum, in agreement with eq 3. However, the calculation of the constants  $Q$  and  $b$  of eq 2 lead to values which deviate from the values used by Mott. The following results were obtained:

#### 1—High purity aluminum:

$Q = 29,000$  cal per gram-atom  
 $b = 10^{-2}$  cgs units

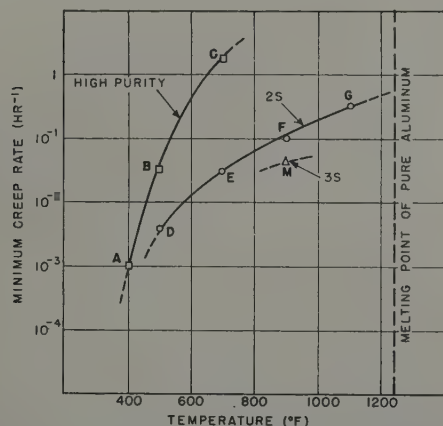


Fig. 17—Logarithm of transition strain rate vs. temperature for high purity, coarse grained 2S and 3S aluminum.

2—2S aluminum:  $Q = 16,000$  cal per gram-atom  
 $b = 10^{-11}$  cgs units

3—Values used by Mott (based on data for 99.991 pct Al)  
 $Q = 35,000$  cal per gram-atom  
 $b = 20$  cgs units

The results show that Mott's theory of grain boundary slip can be applied to an impure solid solution as well as to a high purity material. The critical temperature,  $T_c$ , is markedly affected by the impurity content.

**Temperature Dependence of Creep Rates:** In the absence of structural instabilities, the slope of the straight lines obtained by plotting the logarithm of the stress vs. the logarithm of the minimum creep rate generally increases as the temperature increases. The data obtained for high purity aluminum (Fig. 4) indicate that this rule applies to this material. However, when marked grain growth occurs (at 900° and 1100°F) the slope of the lines decreases.

The data of Fig. 4 for temperatures from 200° to

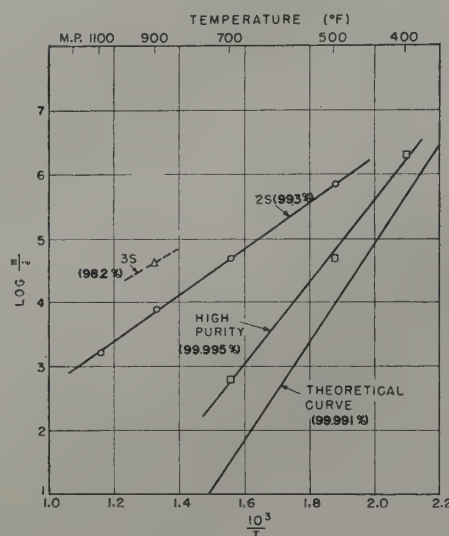


Fig. 18—Logarithm of the ratio of transition stress to transition strain rate  $\frac{\sigma}{\dot{\epsilon}}$  vs. the reciprocal of the absolute temperature of testing, experimental and theoretical curves.

700°F were used to determine the creep rates at constant stress levels. These data are not appreciably affected by grain growth. Both low temperature and high temperature points were taken into consideration since the "breaks" are not sharp enough, in the case of high purity aluminum, to affect the approximate value of the temperature coefficient of creep rates.

The logarithm of the minimum creep rates is plotted vs. the reciprocal of the absolute temperature in Fig. 19. Straight lines should be obtained for each stress level, according to Boltzmann's equation:

$$r = A e^{-Q/RT} \quad [4]$$

where:  $r$  is the rate of a process;  $R$  and  $A$  are constants;  $Q$  is the temperature coefficient; and  $T$ , the absolute temperature.

Only two or three points appear in Fig. 19 for each stress level; therefore, the straight lines do not constitute proof of the validity of eq 4. However, if eq 4 is assumed to be valid, it is possible to de-



termine the approximate value of the temperature coefficient  $Q$  for several stress levels. The values so determined indicate that  $Q$  is a function of the stress according to the equation:

$$Q = M + N \log s \quad [5]$$

where:  $M$  and  $N$  are constants and  $s$  is the applied stress.

This is shown in graphical form in Fig. 20 where the logarithm of the stress was plotted vs.  $Q$ . Eq 5 and Fig. 20 are in agreement with the results obtained by Carreker<sup>14</sup> for platinum wire.

The linear relationship observed in the log-log plot of stress vs. minimum creep rate (Fig. 4) and the validity of eqs 4 and 5 are in agreement with the empirical equation:

$$\log r = a + (b/T - c) (\log s + d) \quad [6]$$

where:  $r$  is the minimum creep rate;  $s$ , the stress;  $T$ , the absolute temperature; and  $a$ ,  $b$ ,  $c$ , and  $d$ , the constants of the material.

Eq 6 was suggested by Servi and Grant<sup>12</sup> based on the analysis of the data obtained by Grant and Bucklin<sup>9</sup> and of other published data.

Fig. 20 does not indicate any sharp change of the

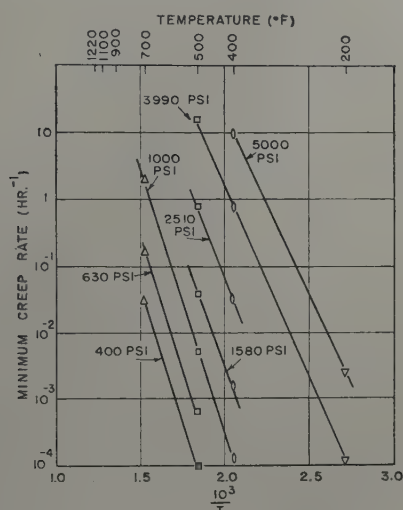


Fig. 19—Logarithm of minimum creep rate at constant stress vs. the reciprocal of the absolute temperature for high purity, coarse grained aluminum.

temperature coefficient  $Q$  at the transition from low temperature to high temperature behavior. Such a negative conclusion is not absolute since the determination of  $Q$  can be done only in an approximate way.

**Primary Creep:** Primary creep was studied for coarse grained, high purity aluminum. When the strain was plotted vs. the cube root of the time, an approximately straight line was obtained during the first stage of creep, in good agreement with the results obtained by Cottrell and Aytekin<sup>18</sup> for zinc. As a first approximation this result is in agreement with Andrade's eq 5:

$$l = l_0 (l + \beta t^{1/3}) e^{\beta t} \quad [7]$$

where:  $l$  is the length of the specimen at time  $t$ ;  $l_0$ , a constant (not necessarily the original length of specimen);  $\beta$ , the coefficient of primary creep; and  $k$ , a coefficient of steady state creep.

The stress dependence of  $\beta$  appears to be similar to the stress dependence of the minimum creep rate, as demonstrated in Fig. 21 where the logarithm of

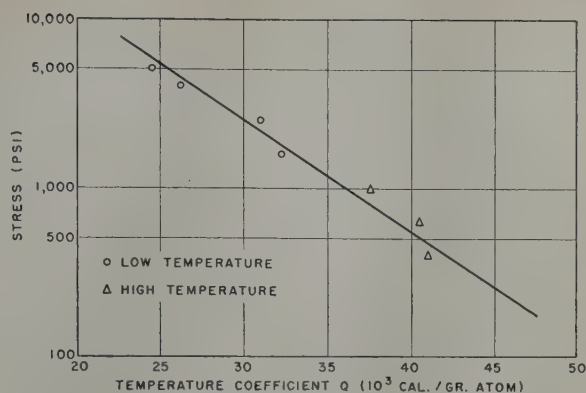


Fig. 20—Logarithm of stress vs. temperature coefficient of strain rate for high purity, coarse grained aluminum.

the stress is plotted vs. the logarithm of  $\beta$  for high purity aluminum tested at 500°F.

The first stage of several creep curves was replotted in other non-conventional ways. Both the log-log and the semilog plots of strain vs. time gave curves of increasing slope. These results indicate that the equations

$$\text{strain} = A t^B \quad [8]$$

and

$$\text{strain} = A + B \log t \quad [9]$$

do not apply to the primary creep of aluminum, at least in the range of temperatures and strain rates investigated.

## Discussion of Results

The results of the present investigation show that the log-log method of plotting creep rate and rupture time data as a function of stress is the most suitable one for analyzing the behavior of aluminum alloys of different purity. The log-log method of plotting reveals structural instabilities, which in the case of aluminum are: 1—the change from low temperature type to high temperature type of deformation, and 2—grain growth.

Change 1 is characterized by the beginning of grain boundary flow. In the case of a high purity material the transition from low temperature to high temperature deformation is revealed by a decrease in creep resistance ("breaks" in the log-log plot of stress vs. minimum creep rate), by metallographic evidence of grain boundary flow, and by the relative strength of coarse and fine grained structures.

In the case of a more impure material the transition also affects the type of fracture which changes from transcrystalline to intercrystalline. The duc-

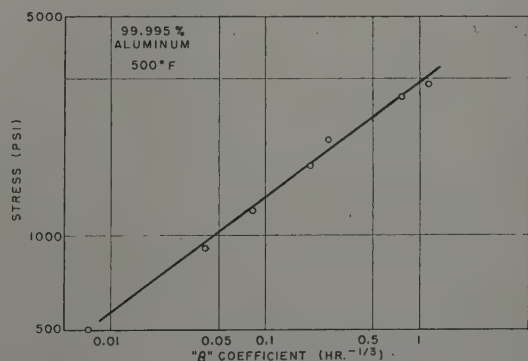


Fig. 21—Log-log plot of stress vs.  $\beta$ , the coefficient of primary creep, for high purity, coarse grained aluminum tested at 500°C.

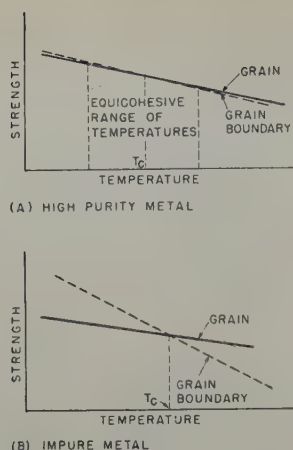


Fig. 22—Strength of the grain and strength of the grain boundary as a function of temperature for high purity and impure metals.

tility of the material decreases as a consequence of intercrystalline cracking.

These conclusions are in good agreement with the results and conclusions obtained by Grant and Bucklin<sup>9</sup> for complex cobalt-base alloys. Similar creep and rupture behavior, at least as far as the transition from low temperature to high temperature type of deformation is concerned, has now been shown to prevail for a high purity metal, two more impure metals, and two complex alloys.

The effect of impurities on the creep and stress rupture properties of metals and especially on the transition from low temperature to high temperature behavior can be interpreted by modifying the theory of equicohesion as follows: it is assumed that two intersecting lines are obtained when the hypothetical "strengths" of the grain and of the grain boundary are plotted vs. the temperature (see Fig. 22). The difference in slope between the two lines is greater for an impure material (Fig. 22B) than for a high purity material (Fig. 22A). The high purity material has a wide range of temperatures where the strengths of the grains and of the grain boundaries are not markedly different. For this reason the decrease in creep resistance observed at the transition from low temperature to high temperature behavior is more marked for an impure than for a high purity metal. For the same reason intercrystalline fracture is not observed in a high purity material tested under high temperature conditions.

Moreover, local recovery and grain boundary migration are more likely to occur in a high purity metal; therefore such a material can undergo a large amount of deformation without cracking along the grain boundaries.

A more impure metal is prone to undergo intercrystalline cracking when tested above the equicohesive temperature,  $T_c$ . Cracking at the grain boundaries gives rise to stress intensification which affects the shape of the creep curve (see Fig. 2), the ductility, and the type of fracture.

### Summary and Conclusions

The results of the present investigation lead to the following conclusions:

1—A transition from low temperature to high temperature-type deformation in metals occurs under proper conditions of testing. The faster the

strain rate, the higher the temperature of transition or the temperature at which grain boundary flow begins.

2—The transition occurs at the point of change in slope of the straight lines which are obtained when the logarithm of the applied stress is plotted vs. the logarithm of the minimum creep rate or the logarithm of the rupture time.

3—At the transition the type of fracture of 2S and 3S aluminum changes from transcrystalline (ductile) to intercrystalline (brittle); the ductility decreases markedly. High purity aluminum does not show a marked change in the type of fracture.

4—The stress and the strain rate at which the transition occurs are related to the temperature as predicted by Mott's theory of grain boundary slip. The constants involved in Mott's equation are affected by the purity of the material.

5—A semilog plot of stress vs. minimum creep rate for high purity aluminum does not give straight lines if a wide range of creep rates is investigated. These results prove that the application of Eyring's theory of activated complex to the creep of metals, as suggested by Dushman et al.<sup>1</sup> and by Kauzmann,<sup>6</sup> is possible only within a narrow range of creep rates as a first approximation.

6—The temperature coefficient,  $Q$ , of creep rates at constant stress follows Boltzmann's equation:

$$\text{rate} = A e^{-Q/RT}$$

$Q$  decreases as the stress increases.

7—Data on primary creep of aluminum are in approximate agreement with Andrade's equation:

$$l = l_0 (1 + \beta t^{1/3}) e^{kt}$$

where  $\beta$ , the coefficient of primary creep, is a function of the applied stress.

### Acknowledgments

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# Structure Observations of Aluminum Deformed in Creep At Elevated Temperatures

by Italo S. Servi and Nicholas J. Grant

THE creep and stress rupture properties of three grades of aluminum have been reported in a previous paper.<sup>1</sup> It was found that the stress coefficient of the creep rate and of the rupture time changes at the transition from low temperature-type to high temperature-type deformation. The transition corresponds to the equicohesion for grains and grain boundaries. In order to support the conclusions obtained from the examination of creep and stress rupture data, the deformed specimens were observed metallographically and a few special tests were conducted. The results of these qualitative observations are given in the present paper.

## Experimental Procedure and Results

Table I gives the types of aluminum specimens.<sup>1</sup>

The creep and stress rupture tests were conducted in simple tension at constant stress. Further details on the experimental techniques have been given.<sup>1</sup>

The test bars were electropolished in a perchloric-acetic mixture before testing and were observed after testing without any further preparation unless otherwise specified. Observations of specimen cross-sections were made after electrolytic polishing and etching. The samples were extended along a direction parallel to the longer side of the micrographs of Figs. 12 through 27.

The log-log plots of stress vs. minimum creep rate for the three grades of aluminum appear in Figs. 1 and 2. The reference numbers on each curve help relate the photographs to the conditions of testing, indicating where high temperature-type deformation and failure prevailed and where low temperature behavior prevailed.

**Deformation of Single Crystals at Very High Temperature:** An annealed, high purity aluminum specimen was slightly strained at one end and re-annealed. A large single crystal was formed at the strained end of the specimen during re-annealing; the other end remained polycrystalline (see Fig. 3). A stress of 50 psi was applied to the cold specimen to avoid loading at 1100°F. The temperature was then raised to 1100°F, kept at 1100°F for 3 hr, and lowered again to room temperature.

Fig. 4 shows the appearance of the specimen after testing. The single crystal deformed by gliding along parallel planes, while the polycrystalline part deformed mainly by grain boundary flow. Some grain growth occurred in the polycrystalline part.

Another high purity specimen, which had two large single crystals at the two ends and a polycrystalline zone in the middle portion, was tested at 1000°F under a stress of 100 psi. The appearance of the sample after test is shown in Fig. 5. Even

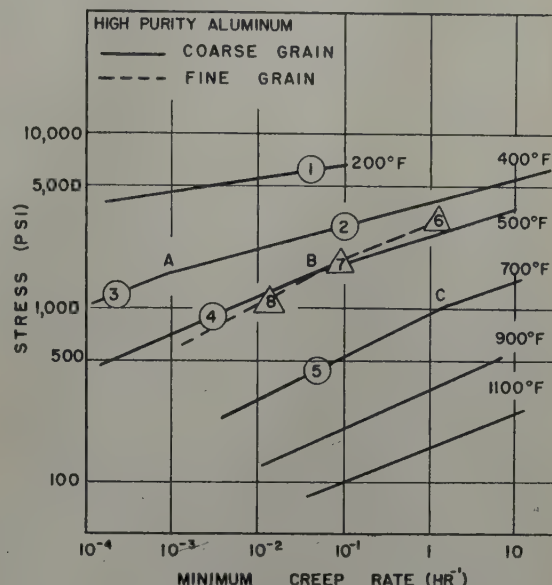


Fig. 1—Log-log plot of stress vs. minimum creep rate for high purity aluminum.

though considerable slip occurred in the single crystals, the fracture occurred in the weaker polycrystalline portion.

**Evidence of Grain Boundary Migration during Creep Testing:** A high purity, coarse grained specimen, which had a large crystal in the middle portion (see Fig. 6) was tested at 700°F under a constant stress of 175 psi for 30 hr. The appearance of the specimen after testing (Fig. 7) indicates that the large crystal deformed by gliding along parallel planes, while the rest of the specimen deformed mainly by grain boundary flow. Microscopic examination showed clear evidence of grain boundary flow and grain boundary migration, an example of

Table I. Types of Aluminum Specimens Used

| Material    | Al Purity, Pct | Grain Size, Mm                                | Designation       |
|-------------|----------------|-----------------------------------------------|-------------------|
| High purity | 99.995         | Single crystals or mixed grain size specimens | Special specimens |
| High purity | 99.995         | 1 to 3                                        | Coarse grained    |
| High purity | 99.995         | 0.05                                          | Fine grained      |
| 2S          | 99.3           | 0.02 to 0.03                                  |                   |
| 3S          | 98.2           | 0.05 to 0.4                                   |                   |

which is presented in Fig. 8. This micrograph can be interpreted as follows: 1—The original grain boundary was located at A. 2—Some grain boundary flow occurred (see displacement of the horizontal scratches.) 3—The grain boundary migrated to the position B.

When a boundary flows, a step is formed on the polished surface of the specimen; the grain boundary, therefore, is revealed as a black line. The apparent "thickness" of the grain boundary depends on the amount of displacement, as well as on the relative orientation of the grain boundary with respect to the polished surface.

A rather complex example of grain boundary flow

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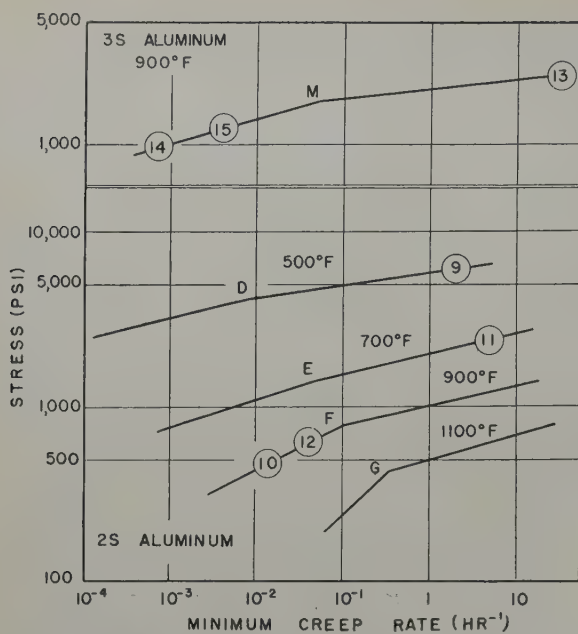
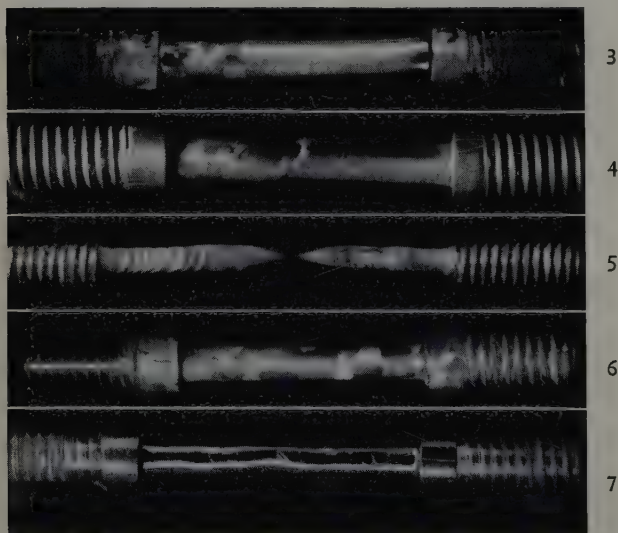


Fig. 2—Log-log plot of stress vs. minimum creep rate for 2S and 3S aluminum.

and grain boundary migration is presented in the composite photograph of Fig. 9. Partial etching revealed the final location of the grain boundaries. A sketch of the micrograph of Fig. 9 is shown in Fig. 10, where the final position of the grain boundaries is indicated by a serrated line.

It seems logical to assume that the initial structure followed the grain boundaries marked A in Fig. 10 and that these boundaries migrated to the final positions, marked F, during the course of the creep test. A trace was left on the polished surface wherever grain boundary flow occurred. The examination of these traces suggests that the migration occurred according to the sequence A-B-C-D-E-F indicated in Fig. 10. However, some of the lines which are visible in Fig. 9 cannot be definitely identified as traces of a grain boundary. For instance,



Figs. 3-7—High purity aluminum specimens.

Fig. 3—Special specimen before testing. Electrolytic polish and etch.

Fig. 4—Same as Fig. 3 after testing at 1100°F as described in text.

Fig. 5—Special specimen after testing under 100 psi at 1000°F. Etched in hydrochloric acid after testing.

Fig. 6—Special specimen before testing. Electrolytic polish and etch.

Fig. 7—Same as Fig. 6 after testing at 700°F.

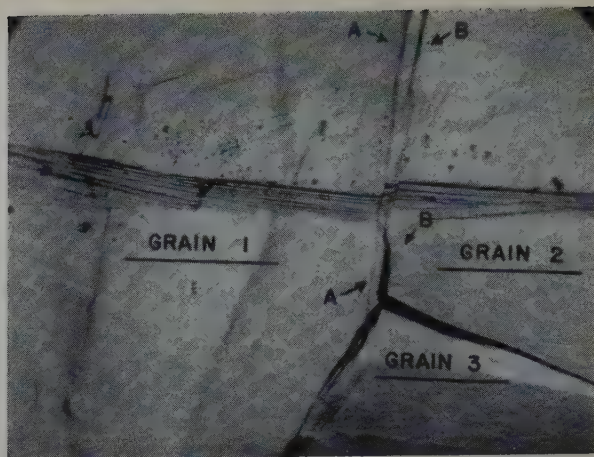


Fig. 8—High purity aluminum. Evidence of grain boundary migration during creep testing. Oblique illumination. X150.

the irregular lines marked C, which appear in the lower part of Fig. 10, can as well be interpreted as deformation bands.

The grain boundaries migrate away from their centers of curvature during creep testing at high temperatures. This phenomenon is of the same type as the grain boundary migration which occurs when cold-worked aluminum is annealed at a suitable temperature, as described by Beck and Sperry.<sup>2</sup>

Step-like grain boundaries were observed after creep testing in a few cases, as shown in Fig. 11. This unusual appearance is probably caused by the combination of flow and migration of two or more grain boundaries.

*Appearance of Deformed High Purity Aluminum as a Function of the Conditions of Testing:* When a coarse grained, high purity aluminum specimen is tested under low temperature conditions, the grain boundaries resist deformation better than the grains, and the fracture occurs along a more or less irregular edge. As the transition from low temperature to high temperature type of deformation is approached, the specimen deforms in a more uniform way and the fracture edge becomes smaller. Under high temperature conditions of testing, the grain boundaries flow, making the grain boundaries appear "thick." The specimen fails by drawing down to a point.

Possibly kinking or other complex types of deformation were active in all the specimens tested.

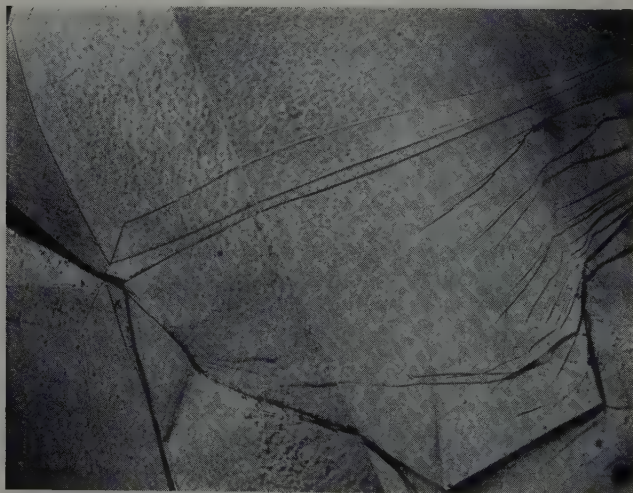


Fig. 9—High purity aluminum. Grain boundary flow and grain boundary migration during creep testing. Oblique illumination. X150.



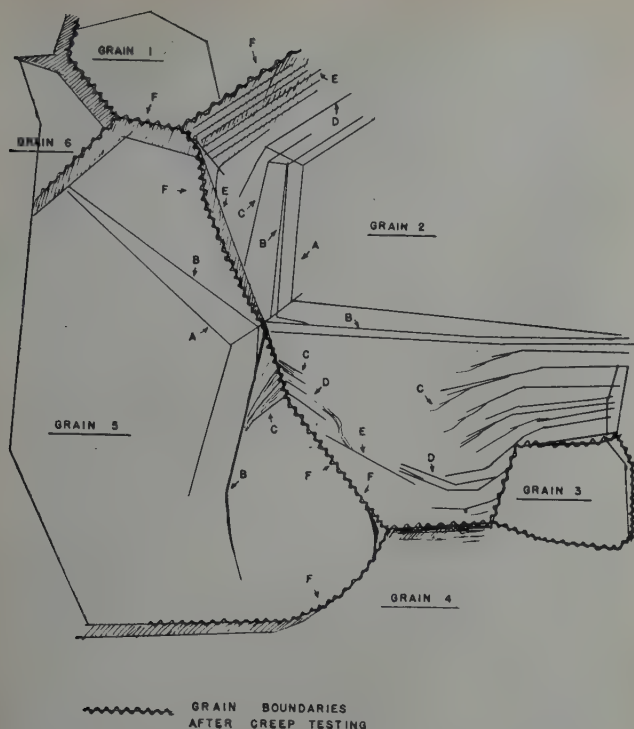


Fig. 10—Sketch of the microstructure of Fig. 9. The direction of the grain boundary migration is indicated by the steps A to F.

However, the qualitative nature of the observations did not permit a clear differentiation between modes of deformation other than grain boundary flow and deformation in the grains. Therefore, all the deformation bands which were observed in the grains have been regarded as "slip bands."

The appearance of the deformed surface changes as a function of the conditions of testing. A few examples are presented in Figs. 12 through 16. Fig. 12 shows a typical "low-temperature" sample, i.e., the grain boundaries did not flow and the deformation occurred in the grains by localized glide along slip bands. Fig. 13 indicates the behavior of the material when the transition is approached. The grain boundaries are still inactive but the deformation of the grains is less localized. The appearance of a specimen tested at high temperature is shown in Fig. 14. There is evidence of grain boundary flow based on grain boundary "thickening," the slip spacing is larger, and a vague cellular appearance is noticed in some parts of the grains. Fig. 15 shows a part of a grain of a specimen tested at still higher temperature. The slip bands are noticeably wavy and a substructure is quite clear. Fig. 16 shows a less localized type of deformation of a high temperature specimen. Wavy slip bands and subgrains are visible. The appearance of fine grained specimens is shown in Figs. 17 through 19.

**Factors Affecting the Spacing of the Slip Bands—"Slipless" Flow:** According to Orowan<sup>8</sup> the minimum slip band spacing is inversely proportional to the applied shear stress according to the equation:

$$d = \frac{G a}{2 \tau} \quad [1]$$

where:  $d$  is the minimum slip spacing;  $G$ , the modulus of rigidity;  $a$ , the interatomic spacing; and  $\tau$ , the shear stress. Since:

$$G/\tau \cong E/\sigma \quad [2]$$

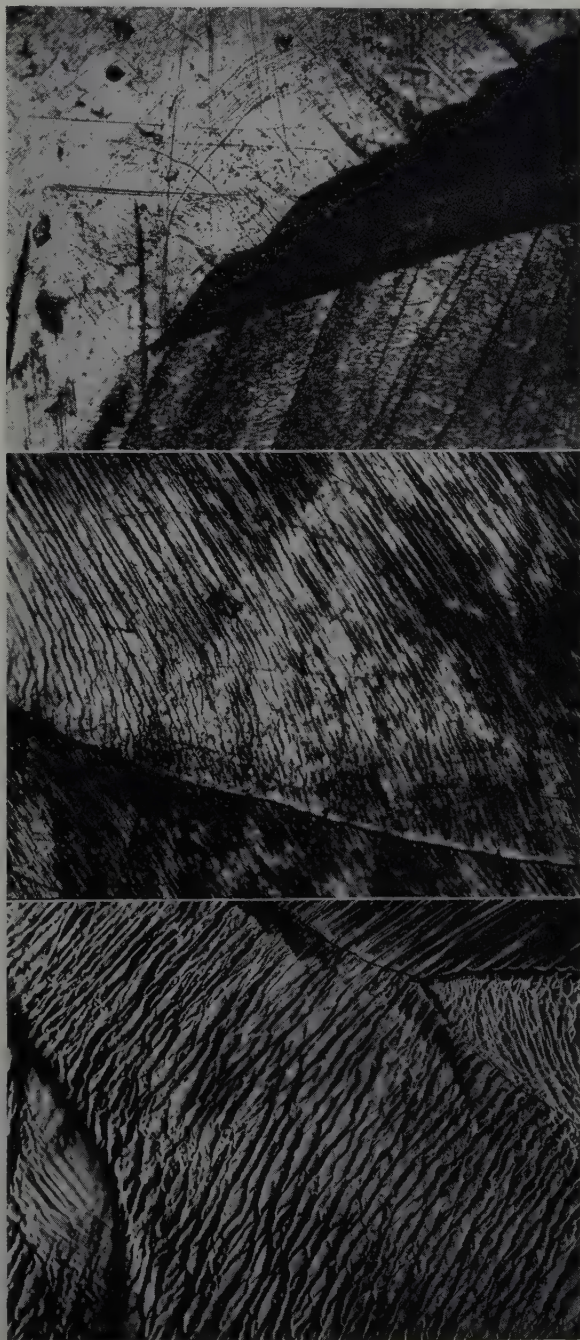
where:  $E$  is the modulus of elasticity, and  $\sigma$ , the tensile stress, in the case of aluminum:

$$d \cong 1/\sigma \quad [3]$$

when  $d$  is expressed in millimeters and  $\sigma$  in psi.

The average slip spacing observed in coarse grained, high purity aluminum, and the average dimension of the "cells," were plotted vs. the applied stress using log-log coordinates (Fig. 20). These data were obtained for samples strained from 15 to 40 pct. Measured values of cell size might vary by a factor of 2 from the averages reported.

The solid line of Fig. 20, which has slope  $-1$ , indicates that the average slip spacing is inversely proportional to the applied stress, at least as a first approximation. The average slip spacing is over 50 times larger than the minimum spacing predicted by Orowan's equation and is in closer agreement with the experimental values obtained by Yama-



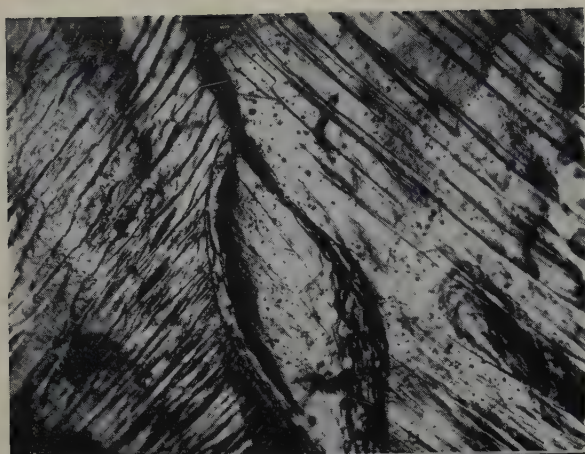
Figs. 11-13—High purity aluminum specimens. X150.

Fig. 11—Tested at 1100°F. Grain boundary flow and grain boundary migration. Oblique illumination.

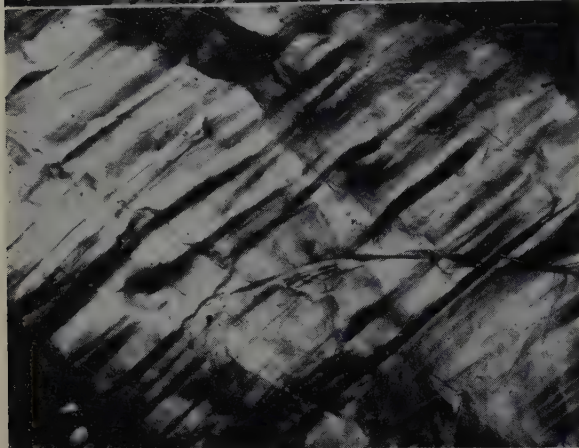
Fig. 12—Coarse grained aluminum at 200°F, 3.4 hr rupture time (point No. 1 of Fig. 1). R.A. is 18 pct.

Fig. 13—Coarse grained aluminum at 400°F, 1.54 hr rupture time (point No. 2 of Fig. 1). R.A. is 15 pct. Oblique illumination.

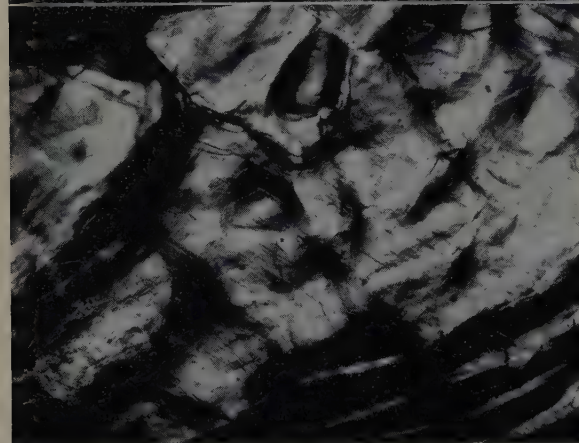




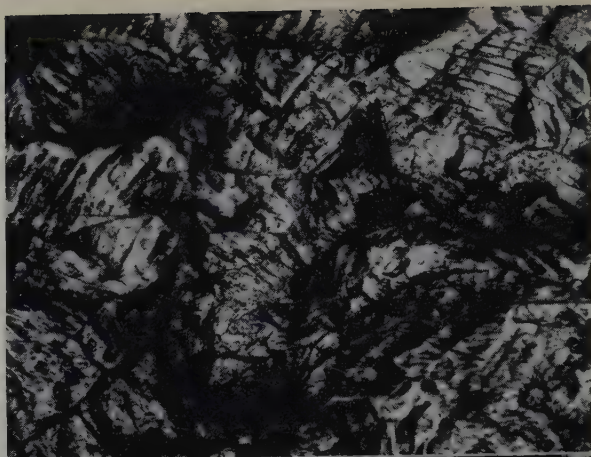
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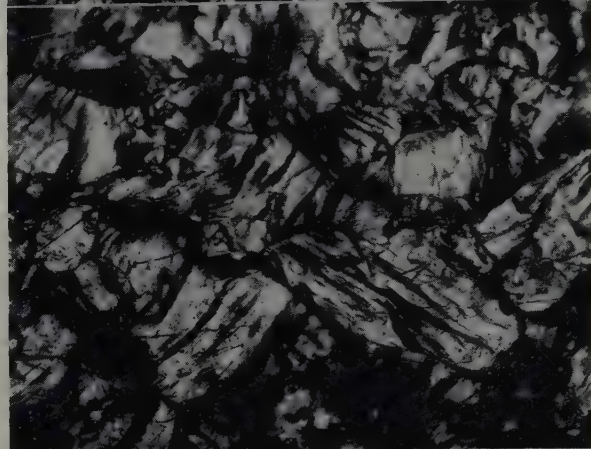
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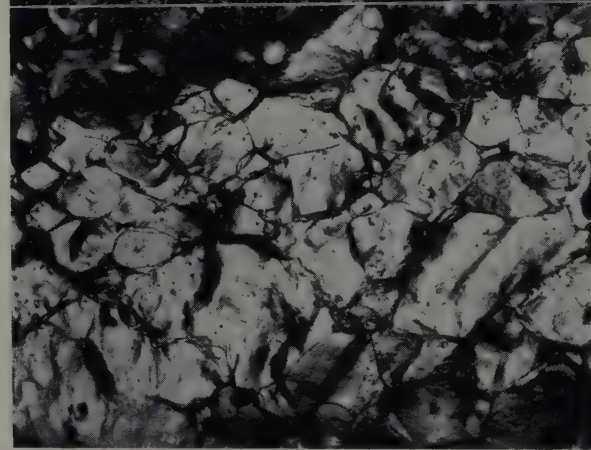
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18



19

Figs. 14-16—High purity, coarse grained aluminum specimens. X150.

Fig. 14—At 400°F, 850 hr rupture time (point No. 3 of Fig. 1).

R.A. is 18 pct.

Fig. 15—At 500°F, 140 hr rupture time (point No. 4 of Fig. 1).

R.A. is 30 pct.

Fig. 16—At 700°F, 13.5 hr rupture time (point No. 5 of Fig. 1).

R.A. is 40 pct.

guchi,<sup>4</sup> as indicated in Fig. 20. This fact can be at least partially justified as follows:

1—The experimental values of this work and of Yamaguchi<sup>4</sup> are the average slip spacings after moderate strain. Orowan's equation predicts the minimum spacing that is obtained after a sufficiently large amount of strain.

2—The experimental values refer to spacing as measured on the surface of the specimen. Orowan's equation predicts the true spacing normal to the slip planes.

The data plotted in Fig. 20 help explain the absence of slip bands (so-called "slipless flow"<sup>5</sup>) observed in some specimens. It was found that single crystals deformed by glide at all temperatures. On the other hand, at the higher temperatures and

Figs. 17-19—High purity, fine grained aluminum specimens. X150.

Fig. 17—At 500°F, 0.44 hr rupture time (point No. 6 of Fig. 1).

1). R.A. is 17 pct.

Fig. 18—At 500°F, 5.43 hr rupture time (point No. 7 of Fig. 1).

1). R.A. is 15 pct.

Fig. 19—At 500°F, 28 hr rupture time (point No. 8 of Fig. 1).

R.A. is 14 pct.

slower strain rates, fine grained specimens deformed by slipless flow. Although this observation was reported long ago by Hanson and Wheeler,<sup>5</sup> it has never been suggested that there is an upper limit of grain size for "slipless flow" to occur. Observations of several specimens lead to the conclusion that this critical grain size is less than the average slip spacing measured on coarser grained specimens for the same value of stress.

For instance, Fig. 19 (at 1200 psi) shows no slip bands in the smaller grains, while one wavy slip band is present in the middle of the larger grains. From Fig. 20 the slip band spacing was calculated for the stress under which the sample of Fig. 19 was tested. At X150 the calculated slip band spacing is 7.5 mm. Fig. 19 indicates that 7.5 mm at X150 is



the order of magnitude of the size of the smaller grains and is approximately the distance between the slip bands and the nearest grain boundaries. The results indicate that grain boundaries have an inhibiting effect on the occurrence of slip bands.

In Fig. 15 there is observed a grain substructure which is delineated by the slip bands and boundaries roughly  $90^\circ$  to the slip bands. This substructure may, in fact, correspond to the cell structure of Wood et al.<sup>6</sup>

Fig. 20 further indicates that the average dimensions of the subgrains observed in several specimens are of the same order of magnitude as the average slip spacing. The dimensions and appearance of the subgrains suggest that they are probably related to the slip system.

*Appearance of Deformed 2S and 3S Al as a Function of the Conditions of Testing:* Similar results to those described for the high purity aluminum were obtained from the observations made on 2S and 3S aluminum. A notable difference in deformation between high purity aluminum and 2S or 3S aluminum is the absence or severe restriction of grain boundary migration in the latter case. For 2S or 3S aluminum, however, intercrystalline cracking is clearly shown in the specimens that were tested under high temperature conditions. Typical micrographs of the surface and of the longitudinal sections of several specimens are presented in Figs. 21 through 28. In Fig. 21 deformation occurred by glide in the grains. There are no grain boundary cracks (2S-low temperature). Fig. 22 shows evidence of grain boundary flow. No slip bands are apparent. The parallel markings in some grains are probably due to cracks in the oxide skin of the surface, perpendicular to direction of applied stress, (2S-high temperature). In Figs. 23 and 24, only Fig. 24, high temperature type behavior, shows intercrystalline cracking. Fig. 23, low temperature type behavior, shows grain elongation and no grain boundary cracks. The cracks in Fig. 24 are widened by the electrolytic polish. In Figs. 25 and 26 the slip is responsible for the def-

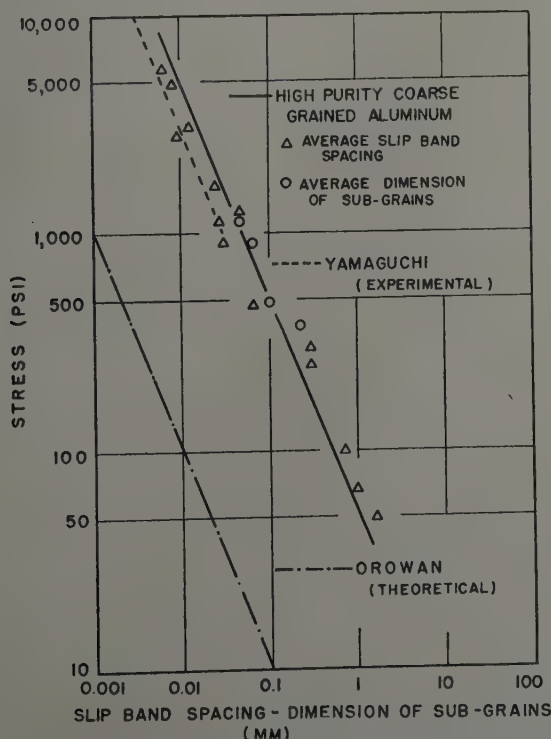
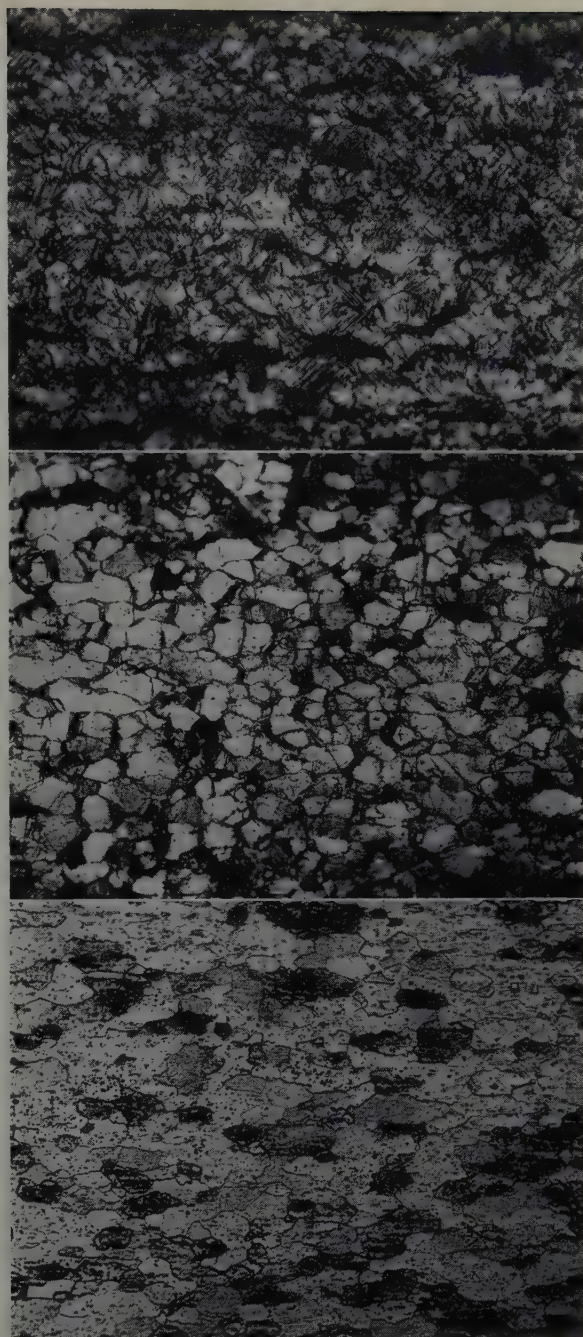


Fig. 20—Log-log plot of stress vs. average slip band spacing and vs. average dimensions of subgrains. Orowan curve calculated from eq 3.

21

22

23



Figs. 21-23—2S aluminum specimens. X150.

Fig. 21—At 500°F, 0.11 hr rupture time (point No. 9 of Fig. 2). R.A. is 26 pct.

Fig. 22—At 900°F, 41.5 hr rupture time (point No. 10 of Fig. 2). R.A. is 31 pct.

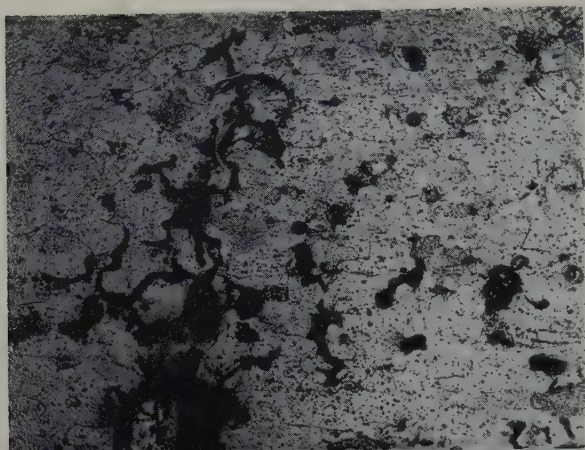
Fig. 23—Longitudinal section at 700°F, 0.09 hr rupture time (point 11 of Fig. 2). Near neck. Electrolytic polish and etch. Oblique illumination.

ormation of 3S aluminum at conditions of low temperature-type behavior. At a slower strain rate, still at 900°F, grain boundary flow and cracks are evident and slip is not evident. Fig. 27, a section of a 3S sample tested for low temperature-type behavior, shows that the grains stand a very large amount of strain without cracking at the grain boundaries at the high strain rates imposed. Near the fracture point recrystallization occurred, probably after failure. Fig. 28, the fracture of a 3S sample (high temperature behavior), is typically intercrystalline. The deformation of the grains is limited. As for Fig. 27, this test is also at 900°F but at much slower strain rates.

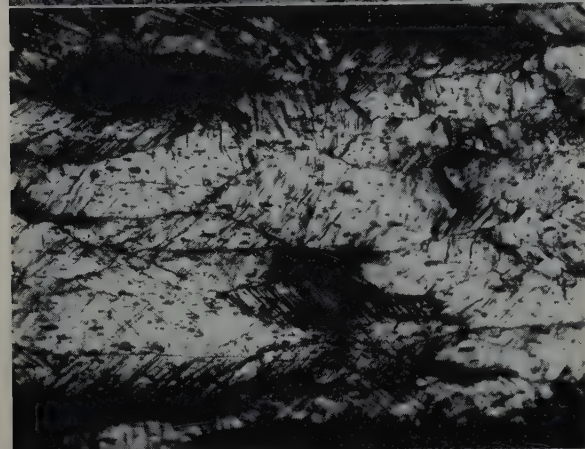
### Summary and Conclusions

1—The conditions of creep testing at which a

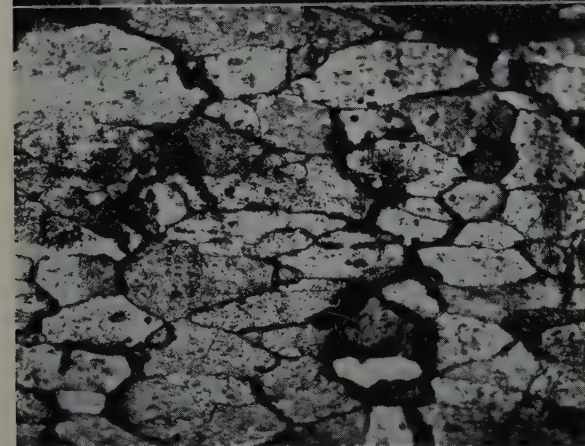




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25



Figs. 24-26—25 aluminum specimens. X150.

Fig. 24—Longitudinal section at 900°F, 18.4 hr rupture time (point No. 12 of Fig. 2). Near fracture. Electrolytic polish and etch.

Fig. 25—At 900°F, 0.01 hr rupture time (point No. 13 of Fig. 2). R.A. is 23 pct.

Fig. 26—At 900°F, 58 hr rupture time (point No. 14 of Fig. 2). R.A. is 5 pct.

change in slope occurs in the log-log plot of stress vs. minimum creep rate or stress vs. rupture time correspond to the beginning of grain boundary flow (equicohesion), but are not directly related to the absence of slip bands.

2—Grain boundary migration occurs in high purity aluminum tested under high temperature conditions. The grain boundaries move away from their center of curvature, as in the case of annealing after cold working.

3—As a first approximation, for specimens deformed 15 to 40 pct, the spacing of the slip bands observed is inversely proportional to the applied stress.

4—Absence of slip bands ("slipless flow") occurs



27



28

Figs. 27-28—3S aluminum, longitudinal section at 900°F.

Fig. 27—0.01 hr rupture time (point No. 13 of Fig. 2). Fracture point. Electrolytic polish and etch. X50.

Fig. 28—11.3 hr rupture time (point No. 15 of Fig. 2). Fracture. Electrolytic polish and etch. X150.

when the grain size is smaller than the average slip spacing observed in a coarser grained specimen tested under the same applied stress.

5—The deformation of aluminum is less localized the higher the temperature, or the slower the strain rate. Subgrains were observed in some specimens tested at high temperature. The dimensions of these subgrains are of the same order of magnitude as the average slip spacing.

6—The dimension, shape and regularity of the subgrains observed in high purity aluminum suggest that the subgrains are related to the slip process or to other less known deformation processes such as kinking. The subgrain formation appears to be the effect, not the cause, of plastic deformation.

#### Acknowledgments

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Thanks are extended to the Aluminum Co. of America for their cooperation in furnishing the three grades of aluminum, suggesting heat treating schedules, and supplying spectrographical analyses.

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# Solubility Relationships in Some of the Ternary Systems Of Refractory Monocarbides

by John T. Norton and A. L. Mowry

Isothermal sections of the pseudo-ternary carbide systems TiC-VC-ZrC, TaC-VC-ZrC, and NbC-VC-ZrC have been examined. The sections contain an inverted U shaped two-phase field whose maximum extent is 77 molecular pct for TiC, 64 pct for TaC, and 51 pct for NbC. Isoparametric lines were determined which show the curvature of the single-phase field and the direction of tie lines in the two-phase field. It was not possible to show any relationship between atom size and the extent of the two-phase field.

PREVIOUS work<sup>1</sup> on the solubility relationship of several pairs of refractory cubic monocarbides from the group TiC, ZrC, VC, NbC, and TaC has shown that, with the exception of the system VC-ZrC, they all form continuous series of solid solutions. It was demonstrated that the limited solubility in the case of VC-ZrC system was primarily a question of the size factor, the size difference between vanadium and zirconium being greater than the limiting value of about 15 pct.

It is interesting to consider the results of combining these isomorphous carbides in groups of three and to determine the isothermal section of the pseudo-ternary diagram at, for instance, 2000°C, a temperature that will assure an equilibrium structure in a reasonable length of time.

In the ternary systems where the three pairs form complete solid solution series, it is probable that the isothermal ternary section would be a single-

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Table I. Metal Atom Diameter Based on Interatomic Distance in Pure Carbide

| Metal | Diameter, A |
|-------|-------------|
| V     | 2.66        |
| Ti    | 2.82        |
| Ta    | 2.95        |
| Nb    | 2.96        |
| Zr    | 3.18        |

phase field, although this is not necessarily the case. However, if one pair of carbides has a very limited solubility, then there must be a two-phase field of some extent, and it is the purpose of the present work to examine the extension of this field and to determine if it can be related to the nature of the third carbide. This condition is fulfilled if the VC-ZrC pair, which has only limited solubility, is combined with TiC, TaC, or NbC.

The relative sizes of the metal atoms undoubtedly play a role in the extent of the single-phase field, and the values obtained from the pure carbides, assuming close-packing between metal and carbon atoms and a carbon atom diameter of 1.54A, are

<sup>1</sup> J. T. Norton and A. L. Mowry: *Trans. AIME* (1949) 185, p. 133; *JOURNAL OF METALS* (February 1949).

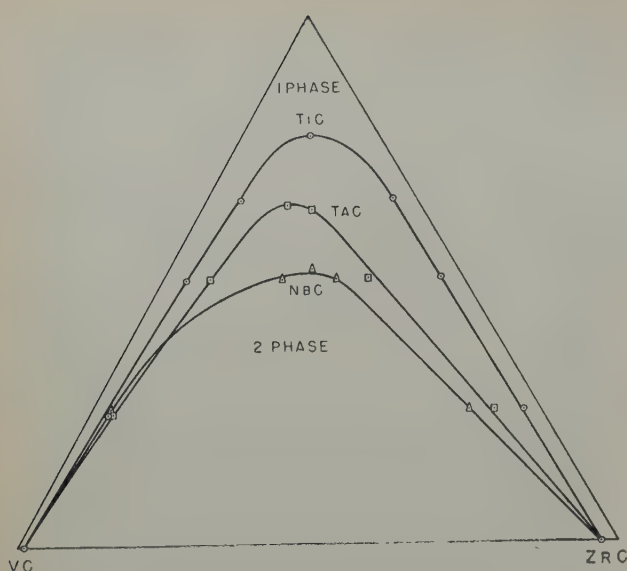


Fig. 1—Composite diagram showing the boundary of the two-phase field for the pseudo-ternary systems, TiC-VC-ZrC, TaC-VC-ZrC, and NbC-VC-ZrC isothermal section at 2000°C.

given in Table I. From these values it would be expected that NbC and TaC would be closely alike in behavior, while TiC would be somewhat different. It is not possible however, to predict whether the single-phase field would be enlarged or reduced.

#### Specimen Preparation

The alloys were prepared by vacuum sintering a mixture of the three separate carbides.

The commercial carbides used were from the same sources as described previously.<sup>1</sup> They were somewhat deficient in combined carbon. Consequently the carbides were weighed out in the quantities required and sufficient additions made of a pure carbon black to give the desired proportions. Some preliminary runs were made that gave indications of the extent of the two-phase field. Then the final compositions were prepared, not only to define the boundary, but also to give some information on the two-phase field. About 30 compositions were used for each ternary system.

The lots were of 10 g each and were mixed in the small laboratory ball mill for 4 hr, using benzene as a dispersing agent. About 0.5 pct of paraffin was added to assist in pressing. After ball milling, the powders were dried and pressed into small cylindrical slugs.

The sintering was carried out in a resistance-heated vacuum furnace with the specimens in graphite containers. The heating time was 12 hr at 2000°C to insure that equilibrium was reached in the specimens. The furnace construction was such that very rapid cooling was obtained as soon as the power was shut off. In the first minute, the temperature dropped approximately 500°C and it is believed that this is sufficiently rapid cooling to retain the structure, which is stable at the sintering temperature. The temperature was controlled manually and was maintained to within  $\pm 20^\circ\text{C}$ .

The slugs sintered into strong and fairly dense

bodies. They were of a clean gray metallic appearance except for the specimens high in TaC, which had a yellowish cast. With one exception, the specimens gave sharp X-ray diffraction lines, indicating that the phases in the alloys were of uniform composition. The exception was a group of three specimens in the NbC-VC-ZrC system close to the boundary where the two phases present were not very different in lattice parameter and seemed to be much slower in reaching equilibrium.

#### X-ray Measurements

Since the purpose of the investigation was to locate the boundary of the two-phase field in the isothermal section, the greater part of the X-ray examination was done with the aid of the Norelco Recording X-ray spectrometer. Experiments on mixed samples of known composition showed that about 2 molecular pct of the vanadium-rich phase would appear as distinct lines in the presence of 98 pct of the zirconium-rich phase. This is the most difficult case and proves that the method is sufficiently sensitive for the purpose. Parameter measurements of the phases were also made from the Norelco records with sufficient accuracy to determine the important features of the diagrams. Where more precision was desired, a Phragmen focusing camera, covering the angular range of Bragg angles from  $60^\circ$  to  $87^\circ$  was employed. Copper  $K_\alpha$  radiation was used throughout the experiments.

The position of points on the phase boundary was determined by noting whether the pattern contained one or two phases. In the region of the boundary, the specimen compositions were quite close together and the X-ray method gave values which probably are within  $\pm 2$  molecular pct. Attempts were made to use a modification of the disappearing phase technique by measuring the ratio of the X-ray line intensities and extrapolating to zero, but the results were no more consistent or precise than the simple observation of the existence of one or two phases

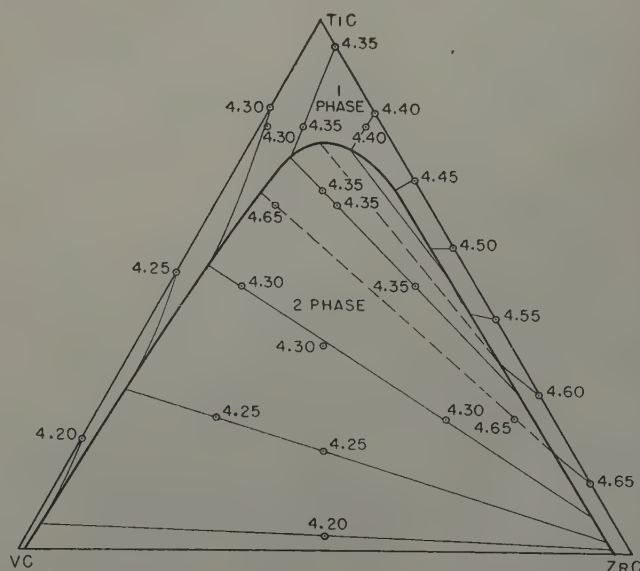


Fig. 2—System TiC-VC-ZrC showing the isoparametric lines. The figures are the lattice parameters of the phases in Angstrom units.



when the compositions were close enough together. At the top of the two-phase field, it is not a case of one phase disappearing but rather two sets of lines merging into one.

If the direction of the tie lines in the two-phase field had been known, and series of alloys prepared lying on these lines, then the precise analytical method of the disappearing phase technique could be applied, but these tie lines, of course, could not be known in advance.

In order to show the distortion of the parametric surface as the single-phase field approaches the two-phase boundary and to find the direction of the tie lines in the two-phase field, the lattice parameters of all of the alloys were measured. The experimental values showed some degree of scatter, and the method used was to plot the measured values along some composition lines of the diagram and draw a smooth curve through the points. The values used in plotting the isoparametric lines were then taken from these smooth curves. The results obtained in this way appear very consistent.

### Results

The results of the phase boundary determinations are shown in Fig. 1 where the curves for the three systems are plotted on a single diagram. The curves are similar in shape and fairly symmetrical. The upper nose of the curve extends to 77 molecular pct in the case of TiC, to 64 pct for TaC, and 51 pct for NbC. On the basis of atom size there appears to be no obvious explanation for the relative positions of these three curves.

The isoparametric lines for the three systems are shown in Figs. 2, 3, and 4. They indicate the fact that the parametric surface of the single-phase region is not plane and that considerable distortion occurs. Compared with the plane surface to be expected from the simple rule of mixtures, the true surface is elevated above this plane as it approaches the boundary of the two-phase field. The greatest distortion is shown in the TiC-VC-ZrC system, especially on the low VC side. In this narrow strip,

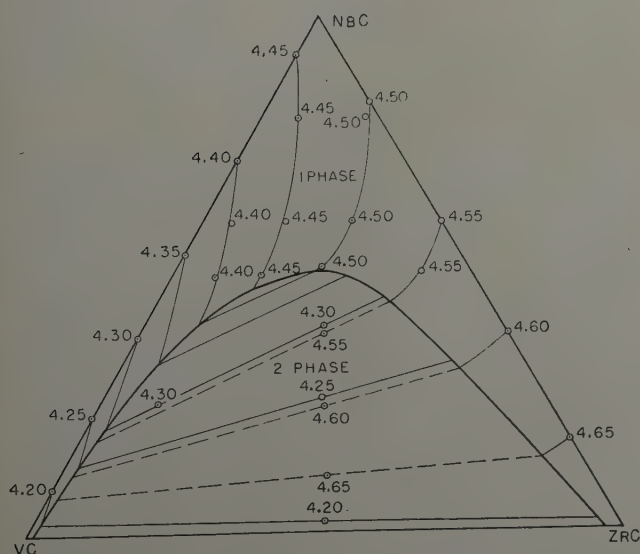


Fig. 3—System NbC-VC-ZrC showing the isoparametric lines. The figures are the lattice parameters of the phases in Angstrom units.

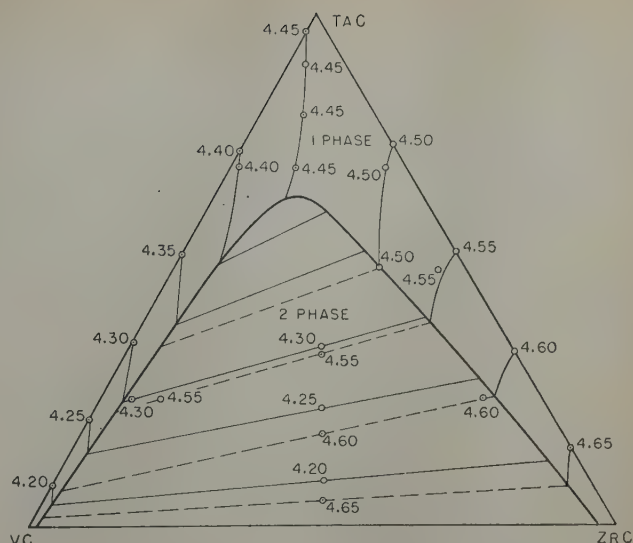


Fig. 4—System TaC-VC-ZrC showing the isoparametric lines. The figures are the lattice parameters of the phases in Angstrom units.

the surface is actually rising when the VC content is increasing, while on the rule of mixture basis it would be falling.

The isoparametric lines in the two-phase fields are actually tie lines, since each point on the phase boundary corresponds to a definite lattice constant. Since the lines are plotted for specific values of the lattice constant, it would not be expected that the lines for the two phases would coincide, but obviously tie lines cannot cross and their trend should be such as to approach the horizontal at the base, that is, the VC-ZrC binary. The experimental results show this trend in the slope in a very definite fashion. In the systems containing TaC and NbC, the slope is downward toward the VC corner while in the TiC system, the slope is toward the ZrC corner.

The positions of the tie lines on the pseudo-ternary diagrams are important because they indicate the directions of the reactions occurring and the phases that will exist together in equilibrium when sintered bodies are made with these carbide combinations.

Unfortunately it does not appear possible to relate the curvature of the single-phase parametric surface or the direction of the tie lines to the properties of the metal atoms involved. In this respect tantalum and niobium resemble one another in behavior more than either resembles titanium. But there is no clear relationship to either atom size or chemical nature. The marked departure of the lattice constants from conditions to be expected from the rule of mixtures suggests that an examination of some of the pseudo ternaries where the three carbides form completely soluble binaries would be of interest. There is a real possibility that a two-phase field would be found.

### Acknowledgments

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# High Temperature Oxidation of Copper-Palladium and Copper-Platinum Alloys

by D. E. Thomas

Oxidation rate constants were determined for Cu-Pd and Cu-Pt alloys as a function of alloy composition and temperature. Reaction products were identified. Relationship between oxidation rate constants and diffusion constants in the reaction zones is discussed.

THE mechanism of oxidation of alloys is considerably more complex and not so well understood as that of pure metals. The oxidation of a one-phase binary alloy of which one component is a noble metal should logically be the simplest case of alloy oxidation, for in this case one is concerned presumably only with the oxidation of the base metal and the diffusion process by which it reaches the reaction site. This had led a number of investigators to study such systems. Probably the earliest work was that of Tammann and Rienäcker<sup>1</sup> on the tarnishing of Cu-Au alloys at temperatures up to 300°C. These alloys oxidize according to the logarithmic law, that is, the film thickness is proportional to the logarithm of the time. The rate of film formation was found to decrease with increasing gold content. Raub and Engel<sup>2</sup> investigated the oxidation of Au-Cu, Cu-Pd, Au-Ag-Cu, Au-Pd-Cu, and Ag-Pd-Cu alloys at 750°C in air. These alloy systems form a continuous series of solid solutions at the temperature of oxidation with the exception of those containing silver.

Au-Cu alloys oxidize parabolically, the rate constant decreasing slowly with increasing gold content up to about 15 atomic pct\* Au, and more rapidly thereafter. An alloy with 14 pct Cu forms only a very thin layer of CuO on the surface and probably also a subscale.† Alloys containing more than 14 pct Cu have scales consisting of CuO and subscales of Cu<sub>2</sub>O embedded in nearly pure gold. The Cu-Pd

alloys obey the parabolic law except for slight deviations for alloys containing 53 and 84 pct Cu. The overall oxidation rate decreases rather smoothly with increasing palladium content. A scale consisting of a thin layer of CuO and a thick layer of Cu<sub>2</sub>O and a subscale of Cu<sub>2</sub>O embedded in nearly pure palladium was observed for alloys containing 84, 53, and 30 pct Cu. An alloy with 19 pct Cu formed only a subscale of CuO embedded in nearly pure palladium, and an 8 pct Cu alloy formed only a thin film which was presumed to be PdO. The ternary alloys considered by Raub and Engel oxidized in much the same way as did the binaries.

Wagner and Grunewald<sup>3</sup> found that Ni-Au alloys, oxidized at 900°C in oxygen, formed a scale of NiO and a subscale containing NiO and gold. The overall oxidation rate increases with increasing gold content, passes through a maximum and then decreases to zero for pure gold. The fact that gold increases the oxidation rate was attributed to "pores" in the scale.

Kubaschewski<sup>4</sup> investigated the air oxidation of alloys of platinum or gold with up to 10 pct Cu or Ni at temperatures in the range 300° to 1550°C. Parabolic behavior was noted for all alloys except Au-Ni, with rates decreasing in the order Au-Cu, Au-Ni, Pt-Ni, Pt-Cu. The diffusion coefficients for the latter three systems are known, and they decrease in the same order. However, activation energies for the oxidation of these alloys do not agree with the activation energies for diffusion in the respective alloy systems.

Kubaschewski and Goldbeck<sup>5</sup> investigated the oxidation of Ni-Pt alloys in air at temperatures of 600°

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\* All subsequent percentage compositions are given in terms of atomic percent.

† The term subscale or zone of internal oxidation here refers to a reaction zone containing two phases, one of which is an oxide, the other metal, situated between the innermost external scale layer and the unoxidized metal.



to 1350°C. As was pointed out in a discussion of their paper, the correct interpretation of their data is that the overall rate constant decreases gradually with increasing platinum content. Their data are not sufficiently precise to test the validity of Wagner's theory of the oxidation of noble metal-base metal alloys.<sup>11</sup>

A study of these publications shows that a subscale is formed under the scale of the base metal, and that the addition of a noble metal to a base metal never results in a disproportionate improvement in the oxidation resistance of the alloy.

Heretofore only overall weight gains have been employed to describe the extent of oxidation, and no quantitative measurements were made on the rates of growth of the individual reaction layers. The role of diffusion in the metal phase and in the oxide phase has not been quantitatively demonstrated for the oxidation of alloys containing noble metals. The present work was undertaken to clarify these points.

### Experimental Procedure

Alloy samples were made from 0.040 to 0.050 in. sheet which was rolled from small vacuum induction melted ingots. Materials used were special carbon-reduced copper obtained from Westinghouse Electric Corp. and c.p. grades of palladium and platinum. The alloy compositions used are listed in Tables I and V. Prior to oxidation, the surfaces of each specimen were polished metallographically, and degreased in alcohol or acetone. Oxidation was carried out in vertical tube furnaces equipped with gasketed pyrex tubes mounted above the furnaces in such a way that the specimen could be lowered from the pyrex tube into the furnace, or raised from the furnace into the pyrex tube, without admitting air to the system. Oxygen was admitted to the system at a pressure slightly in excess of atmospheric pressure through suitable tubulation. Specimens were suspended in the system by means of a platinum wire or a quartz fiber. The specimens were oxidized for various times at temperatures of 850°, 925°, and 1000°C. The alloy systems investigated form a continuous series of solid solutions at these temperatures. The specimens were weighed before and after oxidation. After oxidation the samples were electroplated with a thick layer of copper and sectioned perpendicular to the surface. The cut surface was then polished metallographically and the scale and subscale thicknesses measured from a negative metallographic plate, the electroplated copper serving to delineate sharply the outer scale surface. Because of irregularities in the scale and subscale thickness, it was necessary to compute averages from measurements obtained at regular intervals determined by placing a grid of 10 or 15 lines under the negative. Thus the overall weight gain as well as the scale and subscale thickness was determined.

The scale structure was determined by a combination of optical and X-ray diffraction observations. Cuprous oxide, viewed under the microscope by reflected light, appears blue-gray, and cupric oxide also appears blue-gray, but with a slight pink tinge. Under polarized dark field illumination cuprous oxide appears red and cupric oxide appears nearly black. This permitted the identification of the scale structure for most of the alloys. However, it was found that with increasing palladium content cuprous oxide appeared progressively darker under polarized light, so that it was sometimes difficult to discriminate between cuprous and cupric oxide visually.

Accordingly, samples containing 50 to 85 pct Pd and oxidized at temperatures of 850° and 1000°C were scraped clean of their oxide in order to obtain a powder sample of the scale for analysis by X-ray diffraction using standard techniques. This method of removing the scale yielded a sample which included the scale and also a part of the subscale. Such samples were exposed in a cylindrical powder camera using cobalt radiation with an iron filter. The identity of lines on the film was established by direct comparison with standards run in the same camera. The information so obtained permitted a more definitive visual re-examination of the specimens under the microscope, so that it was possible to identify the oxides of the scale and subscale.

In order to determine the composition of the metal at the scale/subscale interface, the scale was removed in a 10 pct KCN solution from 35 pct Pd alloy samples oxidized at 850° and 1000°C for various times. The descaled samples as well as standard samples were placed in a back-reflection Laue camera, with the scale/subscale interface perpendicular to the incident beam. The palladium content at the scale/subscale interface was then determined from the precision lattice parameters so determined.

The alloy composition in equilibrium with cuprous oxide was determined for the Cu-Pd system. An alloy containing 8.45 pct Pd was selected because the subscale in a fully oxidized specimen of this composition consists of particles of Pd-rich alloy embedded in cuprous oxide, thus making possible a clean separation of phases. Samples of this alloy were oxidized in oxygen at temperatures of 850°, 925°, and 1000°C for times equal to two or three times those required to oxidize the samples to the core, but not long enough to cause an appreciable amount of cupric oxide to grow. Each specimen was powdered and the oxide dissolved in a solution of KCN in glycerine, leaving the Pd-rich particles as a residue. Chemical analyses were then made on this residue.

In order to find out whether a subscale could be produced in Cu-Pd alloys in the absence of an external scale, specimens containing 8.45 and 37.5 pct Pd were packed in a closed pipe with a mixture of copper and cuprous oxide powders and heated for 18 hr at 860°C.

Qualitative chemical analyses were made on scales flaked or abraded from several alloys in order to determine the palladium content of the oxide. One Ni-15 pct Pt alloy was oxidized under the same conditions described above. It was desired only to discover whether a subscale would be formed.

### Scale Structure

*Cu-Pd Alloys:* All of the Cu-Pd alloys investigated formed a scale and a subscale upon oxidation,

Table I. Scale Structures Formed on Cu-Pd Alloys

| Pd Content, Atomic Pct                   | Temperature of Oxidation, °C | Sub-scale              | Scale (Outer/Inner)            |
|------------------------------------------|------------------------------|------------------------|--------------------------------|
| 5.19<br>15.13<br>29.65<br>37.50<br>51.45 | 850 to 1000                  | *α + Cu <sub>2</sub> O | CuO (thin) / Cu <sub>2</sub> O |
|                                          | 1000                         | α + Cu <sub>2</sub> O  | CuO / Cu <sub>2</sub> O        |
|                                          | 850 to 925                   | α + Cu <sub>2</sub> O  | CuO                            |
| 69.92<br>86.50<br>95.14                  | 850 to 1000                  | α + CuO                | CuO / PdO, or CuO / PdO + CuO  |
|                                          | 850 to 1000                  | α + PdO                | PdO                            |
|                                          | 850 to 1000                  | ?                      | PdO film                       |

\* α designates the palladium-rich solid solution.

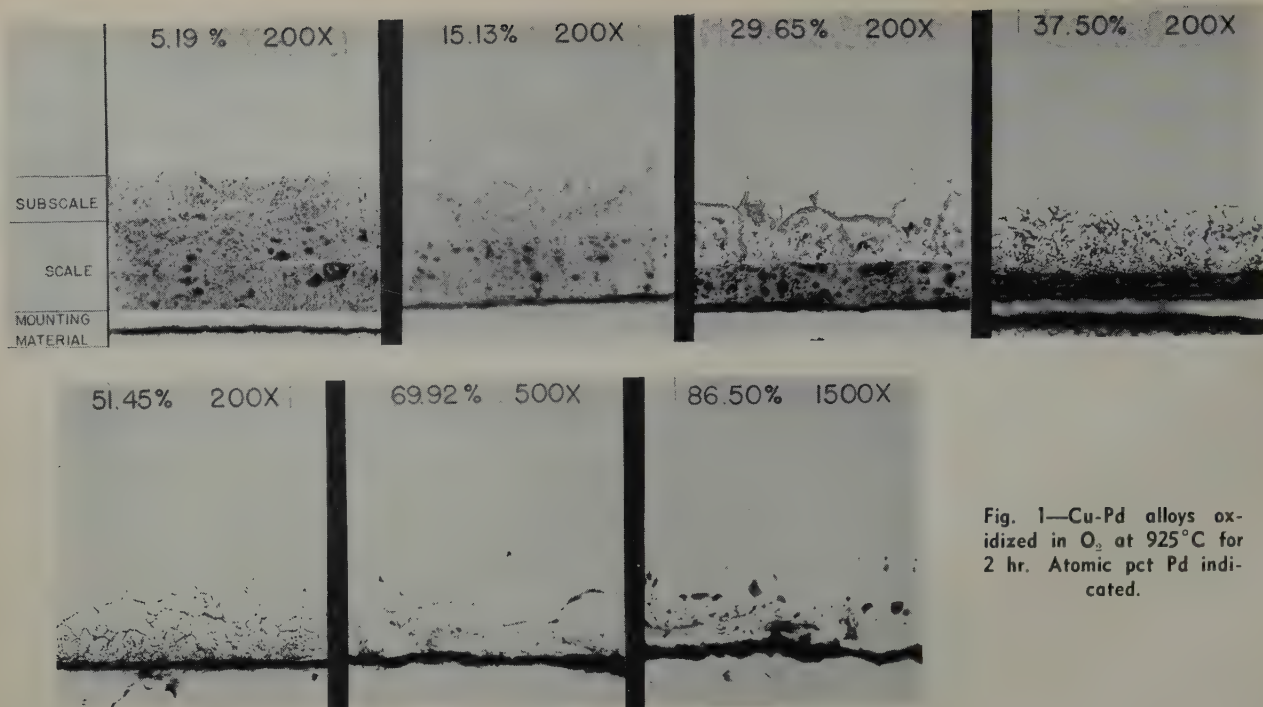


Fig. 1—Cu-Pd alloys oxidized in  $O_2$  at  $925^\circ C$  for 2 hr. Atomic pct Pd indicated.

with the exception of the 95.14 pct Pd alloy, which formed only a thin film of oxide on the surface. No subscale is formed in pure copper. The scale and subscale structures as revealed by visual and X-ray diffraction methods are shown in Table I. It will be noted that the alloys containing less than 50 pct Pd form a subscale of  $\alpha + Cu_2O$  and a  $Cu_2O$  scale layer with a very thin outer layer of  $CuO$ . The scale formed on the 51.45 pct Pd alloy oxidized at  $1000^\circ C$ , however, is about  $\frac{1}{4} CuO$  and  $\frac{3}{4} Cu_2O$ . No  $Cu_2O$  is found on this alloy when oxidized at  $850^\circ$  or  $925^\circ C$ . At 69.92 pct Pd,  $CuO$  appears in the subscale and  $PdO$  appears in the scale. Whether  $PdO$  appears as a distinct layer or as a mixture with  $CuO$  in the scale formed on this alloy could not be determined. Only  $PdO$  was found in the scale and subscale of the 86.5 and 95.14 pct alloys.

It was noted in the X-ray diffraction patterns of the scales removed from the alloys that the  $Cu_2O$  lines and  $CuO$  lines were shifted slightly in the direction corresponding to increasing lattice para-

meter relative to the lines obtained on the pure substances.

Alloy samples containing 8.45 and 37.5 pct Pd heated in a closed container with copper and cuprous oxide powders did not form a zone of internal oxidation.

Chemical analysis of the scale from a 5 pct Pd alloy oxidized at  $925^\circ C$  indicated  $<0.001$  pct Pd, and that removed from a 37.5 pct Pd alloy was found to contain a trace of palladium. Further evidence of palladium in solid solution in the cuprous oxide was afforded by the fact that the characteristic red color of cuprous oxide when viewed under polarized light became darker with increasing palladium content of the alloy. This effect was also observed in the Cu-Pt alloys, but was less pronounced.

The Pd-rich particles which had been separated from specimens oxidized for time periods in excess of those required for complete oxidation to  $Cu_2O$  were found to have the compositions listed in Table II. The compositions given are those in equilibrium with  $Cu_2O$  and oxygen at the indicated temperature.

The composition of the alloy phase in the subscale at the scale/subscale interface as measured by X-ray determination of lattice parameters is shown in Table III. Because the metal phase is saturated with

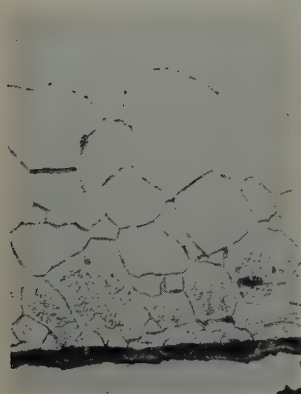


Fig. 2—Micrograph of Cu-51.45 pct Pd alloy oxidized at  $1000^\circ C$  for 2 hr.

Preferential precipitation of  $Cu_2O$  particles is shown at grain boundaries in the subscale. Note how general precipitation lags behind grain boundary precipitation. Unetched. X200.

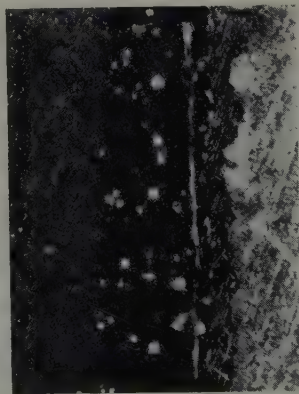


Fig. 3—Micrograph of Cu-37.50 pct Pd alloy oxidized for 8 hr at  $1000^\circ C$ .

Spherical voids are shown in the  $Cu_2O$  scale. Voids appear as interference figures (four leaf clovers). Polarized light, dark field. X75.

Table II. Alloy Compositions in Equilibrium with  $Cu_2O$

| Oxidizing Temperature, $^\circ C$ | Palladium Content, Pct |
|-----------------------------------|------------------------|
| 850                               | 66.0                   |
| 925                               | 68.7                   |
| 1000                              | 68.9                   |

Table III. Alloy Composition at the Scale/Subscale Interface  
Initial Alloy Composition: 37.5 Pct Pd

| Temperature of Oxidation, $^\circ C$ | Time of Oxidation, Hr | Interface Composition, Pct Pd |
|--------------------------------------|-----------------------|-------------------------------|
| 850                                  | 2                     | 64.6                          |
| 850                                  | 4.8                   | 68.8                          |
| 1000                                 | 2                     | 68.5                          |
| 1000                                 | 8                     | 73.3                          |



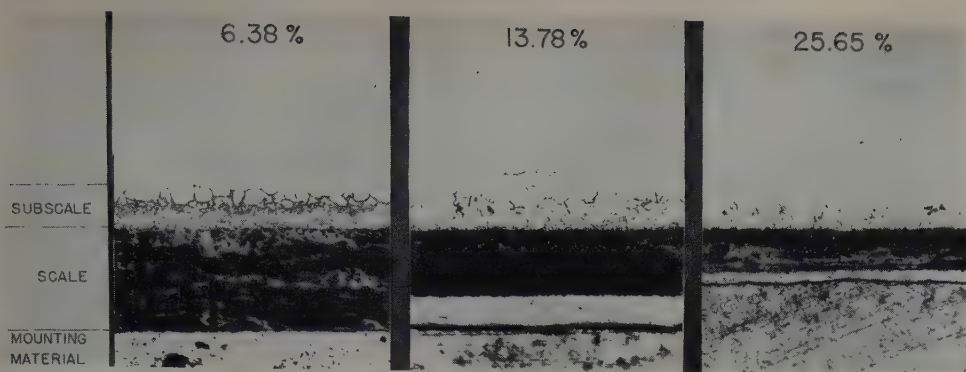


Fig. 4 (left)—Cu-Pt alloys oxidized in  $O_2$  at  $925^\circ C$  for 2 hr. Atomic pct Pt indicated. X200.

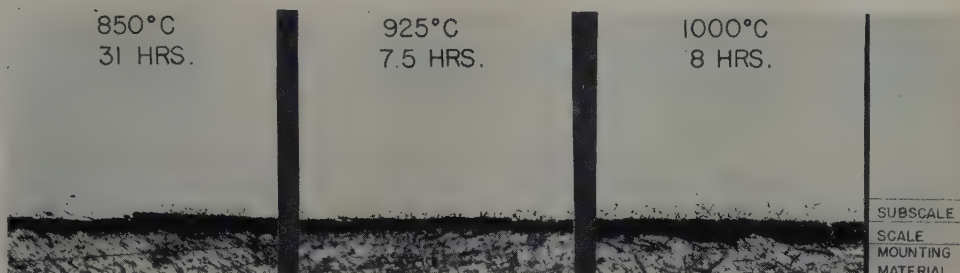


Fig. 5 (right)—Ni-15 atomic pct Pt alloy oxidized in  $O_2$ . X200.

oxygen the values shown are probably higher than the true values. It will be noted that the composition of the alloy phase of the subscale at the subscale/scale interface appears to be dependent upon time. These data cannot be considered conclusive, however, since the depth of penetration of X-rays into the subscale layer yields an average composition of the concentration gradient to this depth. Since the gradient is steeper for short oxidation times, a smaller apparent palladium content would be anticipated.

**Cu-Pt Alloys:** The Cu-Pt alloys investigated (0 to 25 pct Pt) all exhibited a scale of  $Cu_2O$  with a very thin layer of  $CuO$  on the outer side. A subscale was also observed in all samples and consisted of  $Cu_2O$  distributed in a matrix of Pt-rich alloy. It was observed that, in contrast to the Cu-Pd alloys, the  $Cu_2O$  in the scale and subscale darkened only slightly with increasing concentration of noble metal in the alloy when viewed under polarized light.

**Ni-15 Pct Pt Alloy:** A scale of  $NiO$  was observed to form on the Ni-15 pct Pt alloy. There was also formed a subscale consisting of  $NiO$  particles embedded in Pt-rich alloy. This fact has not been re-

ported in previous work on the oxidation of Ni-Pt alloys.<sup>5</sup>

#### Morphology of Scale and Subscale

**Cu-Pd Alloys:** As will be seen subsequently, the external scale thickness increases with increasing temperature and decreases with increasing noble metal content for a given time of oxidation. The extent of the subscale increases with temperature and passes through a maximum as the palladium content increases. The micrographs in Fig. 1 show the structures resulting from oxidation at  $925^\circ C$  for 2 hr as a function of palladium content.

**Subscale:** As may be seen in Fig. 1, the particle size of the subscale oxide decreases from massive in the Cu-rich alloys to very fine in the Pd-rich alloys. The particle size of the subscale oxide increases with the temperature of oxidation. Within a given subscale, larger particles are found near the subscale/alloy interface.

The metal phase of the subscale is continuous in all of the alloys except the 5.19 pct Pd alloy and possibly the 15.13 pct Pd alloy. The relative amount of metal phase in the subscale increases with increasing palladium content, increasing temperature, and distance from the scale/subscale interface.

Table IV. Rate Constants for the Oxidation of Cu-Pd Alloys

| Composition, Atomic Pct | $T$ , $^\circ C$ | Oxygen pressure: 1 atm          |                                    |                                                 |
|-------------------------|------------------|---------------------------------|------------------------------------|-------------------------------------------------|
|                         |                  | $K_s$ , $\frac{cm^2}{per\ Sec}$ | $K_{ss}$ , $\frac{cm^2}{per\ Sec}$ | $K_m$ , $\frac{Mg^2}{cm^4 \cdot Sec}$           |
| Cu                      | 1000             | $2.15 \times 10^{-7}$           | 0                                  | $8.20 \times 10^{-2}$                           |
|                         | 925              | $7.05 \times 10^{-8}$           | 0                                  | $2.90 \times 10^{-2}$                           |
|                         | 850              | $2.67 \times 10^{-8}$           | 0                                  | $1.10 \times 10^{-2}$                           |
| Cu-5.19%Pd              | 1000             | $1.39 \times 10^{-7}$           | $3.20 \times 10^{-8}$              | $6.18 \times 10^{-2}$                           |
|                         | 925              | $3.96 \times 10^{-8}$           | $1.02 \times 10^{-8}$              | $2.51 \times 10^{-2}$                           |
|                         | 850              | $1.18 \times 10^{-8}$           | $1.44 \times 10^{-9}$              | $9.91 \times 10^{-3}$                           |
| Cu-15.13%Pd             | 1000             | $7.10 \times 10^{-8}$           | $5.30 \times 10^{-8}$              | $3.90 \times 10^{-2}$                           |
|                         | 925              | $2.12 \times 10^{-8}$           | $1.54 \times 10^{-8}$              | $1.51 \times 10^{-2}$                           |
|                         | 850              | $8.85 \times 10^{-9}$           | $8.34 \times 10^{-9}$              | $6.70 \times 10^{-3}$                           |
| Cu-29.65%Pd             | 1000             | $2.61 \times 10^{-8}$           | $5.93 \times 10^{-8}$              | $1.78 \times 10^{-2}$                           |
|                         | 925              | $8.05 \times 10^{-9}$           | $1.21 \times 10^{-8}$              | $6.25 \times 10^{-3}$                           |
|                         | 850              | $3.02 \times 10^{-9}$           | $4.58 \times 10^{-9}$              | $2.38 \times 10^{-3}$                           |
| Cu-37.50%Pd             | 1000             | $8.80 \times 10^{-9}$           | $7.49 \times 10^{-8}$              | $8.51 \times 10^{-3}$                           |
|                         | 925              | $2.64 \times 10^{-9}$           | $1.56 \times 10^{-8}$              | $2.29 \times 10^{-3}$                           |
|                         | 850              | $9.55 \times 10^{-10}$          | $5.91 \times 10^{-9}$              | $8.68 \times 10^{-4}$                           |
| Cu-51.45%Pd             | 1000             | $1.03 \times 10^{-9}$           | $1.35 \times 10^{-7}$              | $2.58 \times 10^{-3}$                           |
|                         | 925              | $1.96 \times 10^{-10}$          | $1.35 \times 10^{-8}$              | $5.38 \times 10^{-4}$                           |
|                         | 850              | $7.65 \times 10^{-11}$          | $4.16 \times 10^{-9}$              | $2.31 \times 10^{-4}$                           |
| Cu-69.92%Pd             | 1000             | $8.15 \times 10^{-11}$          | $1.39 \times 10^{-8}$              | $8.75 \times 10^{-4}$                           |
|                         | 925              | $4.31 \times 10^{-11}$          | $1.91 \times 10^{-9}$              | $2.02 \times 10^{-4}$                           |
|                         | 850              | $2.15 \times 10^{-11}$          | $8.69 \times 10^{-10}$             | $7.29 \times 10^{-5}$                           |
| Cu-86.50%Pd             | 1000             |                                 |                                    | $5.90 \times 10^{-5}$ ( $3.19 \times 10^{-6}$ ) |
|                         | 925              | $2.33 \times 10^{-12}$          | $7.50 \times 10^{-10}$             | $2.46 \times 10^{-5}$                           |
|                         | 850              | $1.61 \times 10^{-12}$          | $6.25 \times 10^{-11}$             | $8.68 \times 10^{-6}$                           |

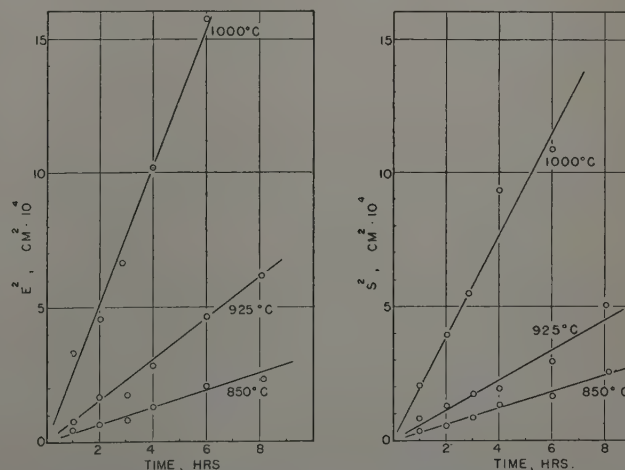


Fig. 6—Square of the scale and subscale thickness vs. time for Cu-15.13 atomic pct Pd alloy oxidized in  $O_2$ .

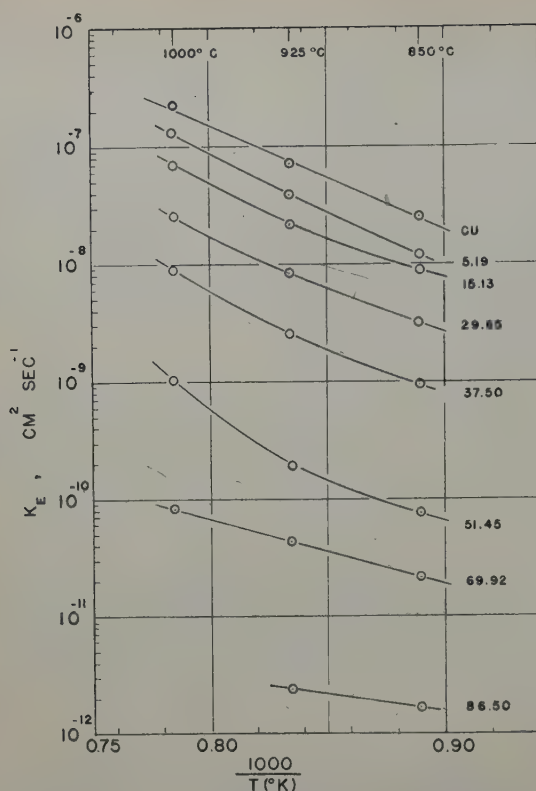


Fig. 7—Temperature dependence of the parabolic rate constant based on scale thickness for the oxidation of Cu-Pd alloys. Atomic pct Pd indicated.

There is a definite tendency for the subscale oxide to precipitate at grain boundaries, becoming more pronounced with increasing palladium content. The grain boundary effect is typified in Fig. 2. The grain boundaries near the scale/subscale interface are not usually as well defined by oxide particles as those near the subscale/alloy interface. This suggests that there is a considerable amount of rearrangement of the oxide particles which formed early.

It will be noted in Fig. 2 that grain boundaries nearer the scale/subscale interface contain more

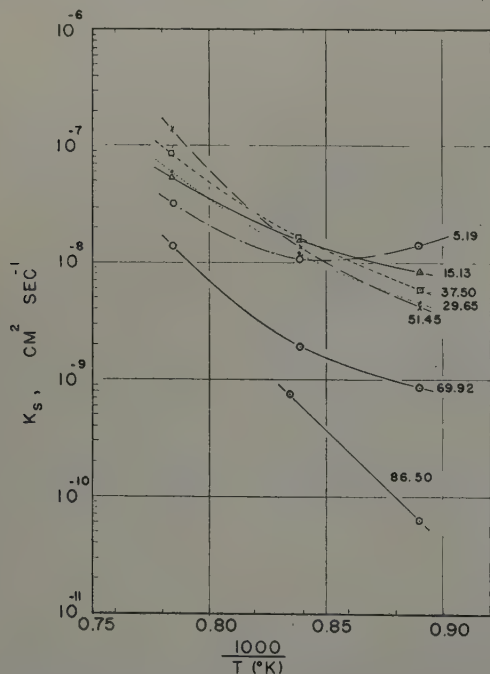


Fig. 8—Temperature dependence of the parabolic rate constant for subscale thickness for Cu-Pd alloys. Atomic pct Pd indicated.

oxide particles than those near the subscale/alloy interface, suggesting that the formation of grain boundary oxide results from the formation of a few nuclei which grow in the grain boundary until they impinge.

There is a tendency for plate-like oxide particles to be thicker when oriented parallel to the specimen surface. This is most pronounced in the Pd-rich alloys.

**Scale:** The grain size of the external scale is in general of the same order of magnitude as the scale thickness. No systematic measurements were made, however. When a CuO layer of appreciable thick-

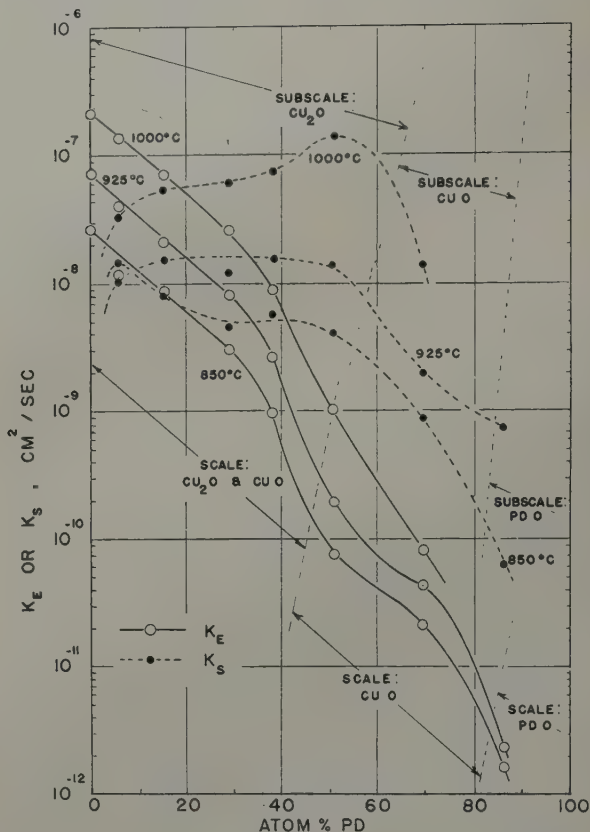


Fig. 9—Parabolic rate constants  $K_E$  and  $K_S$  as a function of alloy composition. Cu-Pd alloys oxidized in  $O_2$ , 1 atm pressure.

ness is formed, the surface of the oxide takes on a rough grained appearance.

An increasing number of spherical voids in the  $Cu_2O$  scale was observed with increasing palladium content and with increasing temperature. The number of voids varied from a few to 5 or 6 per field at 500X. The maximum number was found in the 37.5 pct Pd alloy. Above this palladium content no voids were found. Fig. 3 shows voids in the scale formed on a 37.5 pct Pd alloy.

**Cu-Pt Alloys:** The microstructures shown in Fig. 4 for the oxidation of Cu-Pt alloys at 925°C for 2 hr are typical of those found at the other temperatures.

The same tendencies noted for the particle size of the subscale oxide in the Cu-Pd alloys were noted for the Cu-Pt alloys. In general the particle size was finer in the subscale of the Cu-Pt alloys. The metal phase is continuous in the subscale of all the Cu-Pt alloys investigated, and the tendency for grain boundary precipitation is more pronounced in the Cu-Pt system than in the Cu-Pd system at comparable noble metal concentration.

The morphological features of the scales formed



on Cu-Pt alloys are similar to those formed on Cu-Pd alloys.

**Ni-15 Pct Pt Alloy:** The scale and subscale were quite irregular in thickness. The particle size of the NiO in the subscale was relatively fine and increased with increasing temperature of oxidation. Fig. 5 shows that there is no tendency toward grain boundary precipitation in the subscale and that the metal phase is continuous.

### Kinetics

The parabolic law was found to describe the oxidation of most of the alloys investigated. Since the thickness of the scale and subscale as well as the

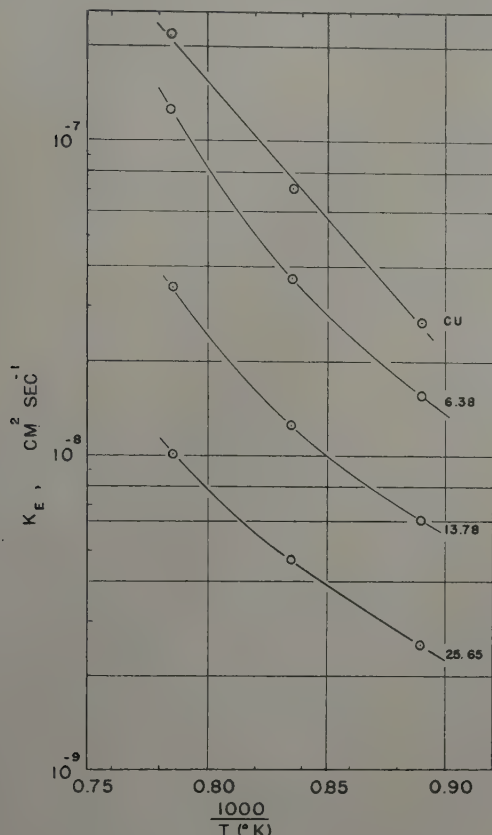


Fig. 10—Temperature dependence of the parabolic rate constant based on scale thickness for the oxidation of Cu-Pt alloys. Atomic pct Pt indicated.

overall weight gain was observed, the data were treated using the following equations:

$$\Delta m^2 = K_m t \quad [1]$$

$$E^2 = K_E t \quad [2]$$

$$S^2 = K_S t \quad [3]$$

where  $\Delta m$  is the weight gain in mg per  $\text{cm}^2$ ;  $E$ , the external scale thickness in cm;  $S$ , the subscale thickness in cm;  $t$ , the time in sec; and  $K$ , the respective parabolic rate constant.

**Cu-Pd Alloys:** Typical curves showing the square of the external scale thickness and the square of the subscale thickness plotted against time are shown in Fig. 6. From such curves the parabolic rate constants were calculated for the scale, the subscale, and the gross weight gain. These are given in Table IV and need no comment other than to point out the anomalous behavior of the 86.5 pct Pd alloy oxidized at 1000°C. It was found that some specimens of this alloy formed a film while others formed a scale. No correlation of this behavior could be made with minor variations in the experimental conditions.

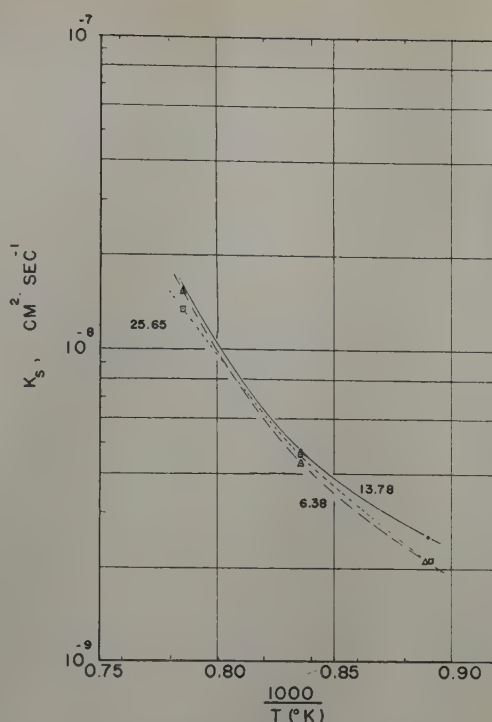


Fig. 11—Temperature dependence of the parabolic rate constant for subscale thickness for Cu-Pt alloys. Atomic pct Pt indicated.

The temperature dependence of the rate constants,  $K_E$  and  $K_S$ , is shown in Figs. 7 and 8 wherein the logarithms of the respective rate constants have been plotted against the reciprocal of the absolute temperature. It is to be noted that a straight line results only for  $K_E$  for pure copper and for the 69.9 pct Pd alloy. Thus in most cases the activation energy increases with increasing temperature. The temperature dependence of  $K_m$  is similar to that for  $K_E$ .

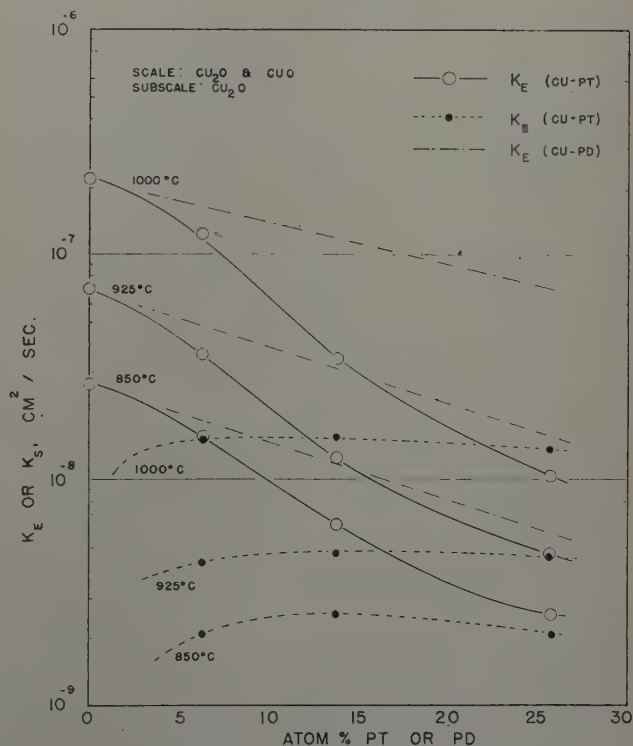


Fig. 12—Parabolic rate constants  $K_E$  and  $K_S$  as functions of alloy composition. Cu-Pt alloys oxidized in  $\text{O}_2$ , 1 atm pressure.  $K_E$  for Cu-Pd alloys is shown for comparison.

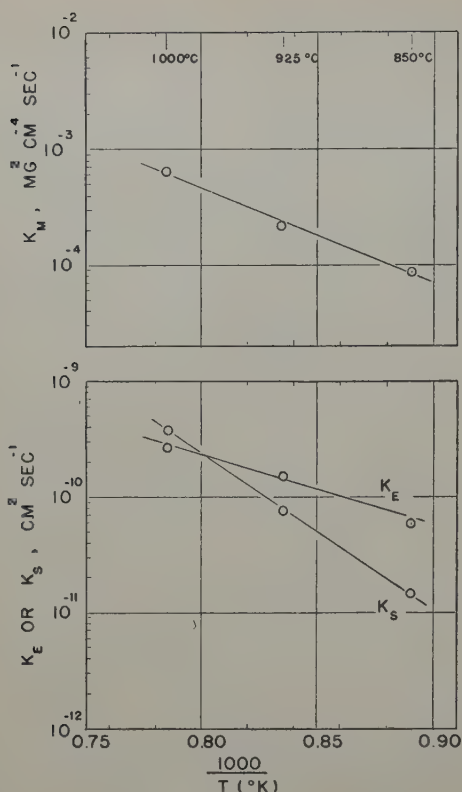


Fig. 13—Temperature dependence of the parabolic rate constants  $K_m$ ,  $K_E$ , and  $K_S$  for the oxidation of Ni-15 atomic pct Pt alloys.

The dependence of  $K_E$  and  $K_S$  upon the palladium content is illustrated in Fig. 9, in which the rate constants are plotted on a log scale for convenience. It is seen that  $\log K_E$  decreases linearly with increasing palladium content up to about 25 pct Pd. Subsequently,  $\log K_E$  begins to drop off more rapidly until there is only CuO in the external scale, at which juncture an inflection occurs (40 to 50 pct Pd). With further increase in palladium content, the rate at which  $\log K_E$  drops off appears to decrease until PdO appears as the external scale at a palladium content between 70 and 85 pct. With the onset of the PdO scale,  $\log K_E$  undergoes a rather

sharp decrease. The behavior is essentially the same at the three temperatures investigated.

The shape of the curve of  $\log K_S$  vs. palladium content varies considerably with temperature, with maxima occurring at 50 pct Pd at 1000°C, 15 to 20 pct Pd at 925°C, and 5 pct Pd at 850°C. The maxima occur in the concentration range in which the subscale oxide is  $\text{Cu}_2\text{O}$  and the external scale is largely  $\text{Cu}_2\text{O}$ .

**Cu-Pt Alloys:** The rate constants,  $K_E$ ,  $K_S$ , and  $K_m$ , for the Cu-Pt alloys are listed in Table V. In some instances deviations from parabolic behavior were found after 6 hr. In such cases the rate constant was calculated from the data up to 6 hr oxidation time.

The temperature dependence of  $K_E$  and  $K_S$  is shown in Figs. 10 and 11, respectively. The activation energy for  $K_E$  and  $K_S$  is seen to increase with temperature. A similar temperature dependence for  $K_m$  was found.

The effect of platinum content upon  $K_E$  and  $K_S$  is shown in Fig. 12.  $\log K_E$  decreases with increasing palladium content in a complex way. The corresponding curves for Cu-Pd alloys are also indicated in Fig. 11, and it is seen that  $K_E$  is greater for the Cu-Pd alloys than for Cu-Pt alloys at the same temperature and composition.

The  $\log K_S$  vs. platinum curve passes through a broad maximum at about 14 pct Pt, which does not depend upon the temperature.

**Ni-15 Pct Pt Alloy:** The data for weight gain, scale thickness, and subscale thickness showed a great deal of scatter. It was therefore necessary to assume parabolic behavior and to calculate the rate constants giving the best fit.  $K_E$ ,  $K_S$ , and  $K_m$  are listed in Table V. The  $K_E$  values for pure nickel in Table V are calculated from the  $K_m$  values given by Kubaschewski and Goldbeck.<sup>6</sup> In view of the scattering of the present data and that of the Kubaschewski and Goldbeck data, no statement can be made concerning the effect of platinum on the rate constants.

The effect of temperature upon  $K_E$  and  $K_S$  is shown in Fig. 13. The activation energy for  $K_E$  is 29,900 cal per mol and for  $K_S$  is 66,400 cal per mol.

## Discussion of Results

**Scale Structure:** It is of interest to consider the several sequences of phases observed for the oxidation of Cu-Pd alloys in relation to the ternary equilibrium diagram involving copper, palladium, and oxygen. Such a treatment for the internal oxidation of the  $\alpha$  solid solutions of copper has been discussed in detail by Rhines.<sup>7</sup> Fig. 14 is a schematic representation of an isothermal section of the Cu-Pd-O system in which the extent of solid solubility has been exaggerated for clarity. One and two-phase fields in the diagram correspond to one and two-phase layers in the oxidized specimen, while three-phase fields in the diagram correspond to interfaces in the specimen. Reference to Table I shows that five distinct modes of oxidation were observed for the Cu-Pd alloys. The locus of compositions is shown schematically in Fig. 14 for each of these modes. Consider case A, which represents the alloys containing up to 37.5 pct Pd. The initial copper concentration is  $C_0$ , and, as one passes toward the outside of the specimen, the copper concentration decreases until a value  $C_1$  is reached at the alloy/subscale interface. Upon traversing the subscale region, the locus of average compositions in the subscale is indicated by the line connecting  $C_1$  and  $\text{Cu}_2\text{O}$ .

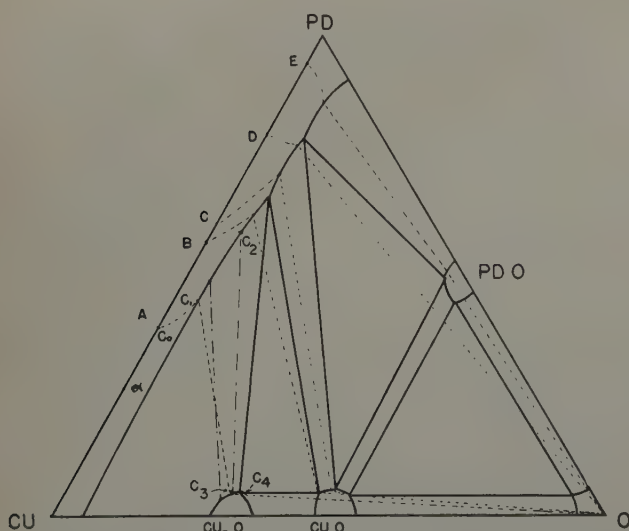


Fig. 14—Isothermal section of the Cu-Pd-O equilibrium diagram. Distorted scale.



The composition of alloy and oxide at a given position in the subscale is given by the ends of the tie line passing through the average composition at this position. Thus, at the subscale/scale interface the alloy composition is given by  $C_2$  and the oxide composition by  $C_3$ . Upon passing through the  $\text{Cu}_2\text{O}$  scale the copper concentration will decrease from  $C_3$  to  $C_4$ . From  $C_4$  the locus of compositions passes through the  $\text{Cu}_2\text{O} + \text{CuO}$  field. This structure, however, was not found, which may mean simply that this reaction layer was too thin to resolve. The relationship of the above composition loci to the kinetics involved may be seen by comparison with Fig. 18. The above reasoning may be applied to the other modes of oxidation indicated by B, C, D, and E, in Fig. 14. Mode A is to be considered typical also for the Cu-Pt alloys studied.

It was shown that palladium or platinum is taken into solid solution in cuprous oxide. This fact appears to be the crux of the subscale question. The effect of palladium or platinum addition to cuprous oxide is to increase the partial pressure of oxygen in equilibrium with the oxide, in view of the fact that alloys packed in  $\text{Cu}_2\text{O}$  powder do not form subscales while the same alloys do form a subscale under a  $\text{Cu}_2\text{O}$  scale containing a small amount of noble metal. It is seen in Fig. 15 that at the scale/subscale interface the palladium (or platinum) content in the metal phase is higher than at any other place. Hence the oxide in contact with this metal phase must have more palladium (or platinum) in solid solution, and consequently a higher partial pressure of oxygen,  $P_{\text{O}_2}^s$ . However, at the alloy/subscale interface the palladium concentration is less than at the scale/subscale interface, and the pressure of oxygen at the alloy/subscale interface is thus smaller than  $P_{\text{O}_2}^s$ . The difference,  $P_{\text{O}_2}^s - P_{\text{O}_2}^i$ , represents the driving force for diffusion of oxygen across the subscale. The composition of the oxide in the subscale is a function of the distance from the scale/subscale interface, being higher in palladium at the scale/subscale interface. These relationships can be seen by considering the tie lines in the  $\alpha + \text{Cu}_2\text{O}$  field in Fig. 14. It is apparent then that if  $\text{Cu}_2\text{O}$  could not take palladium into solution, there could be no gradient of oxygen pressure across the two-phase field, hence no subscale. This may be general for the oxidation of binary alloys with one noble component.

**Morphology:** The formation of the subscale may properly be thought of as a nucleation and growth process taking place isothermally under the influence of diffusion currents. The number of nuclei for the subscale oxide should depend largely upon the concentration of oxygen in the metal phase, since there is always a relatively abundant supply of copper atoms. It is to be expected that the solubility of oxygen should increase with increasing noble metal content, so that there should be a greater number of oxygen atoms available to form nuclei, hence a larger number of particles and a smaller particle size.

The grain boundary preference is probably primarily a result of preferential nucleation of the oxide precipitate at the grain boundaries, rather than higher rates of diffusion in the grain bound-

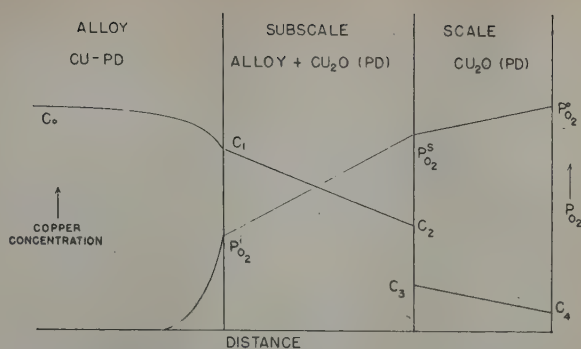


Fig. 15—Schematic representation of the partial pressure of oxygen as a function of distance, Cu-Pd alloys.

aries, since the effect of temperature is opposite to that expected in the latter case.

The presence of voids in the  $\text{Cu}_2\text{O}$  scale may be tentatively explained in the following way. Copper can diffuse toward the scale through the metal and the oxide phases of the subscale, while the noble metal can diffuse in the opposite direction only through the metal phase. Thus in the metal phase of the subscale there is an unequal transport of copper and noble metal, which is believed to be possible only if a stream of lattice vacancies flows in the direction opposite to that of the most rapidly diffusing component, here the noble metal. The vacancies, having passed through the subscale may then enter the scale, and there collect to form voids.

**Kinetics:** In considering the treatment of the kinetic data it is appropriate to inquire into the possibility of the application of Wagner's analysis, since it would presumably be applicable if the amount of oxygen in the subscale were negligible compared to the total amount involved in the oxidation process. The fraction of oxide in the external scale,  $\alpha$ , is given by:

$$\alpha = \sigma \sqrt{\frac{K_E}{K_m}} \quad [4]$$

where  $\sigma$  is a constant calculated from densities and molecular weights. Values of  $\alpha$  are shown in Figs. 16 and 17, where it may be seen that the relative amount of oxygen involved in the subscale increases with increasing noble metal content, and may reach a value of 2/3; i.e.,  $\alpha = 0.33$ . Evidently the relative amount of oxygen in the subscale is not negligibly small, and Wagner's analysis cannot be applied, at least not in its entirety.

Kinetic equations for the growth of scale and subscale were derived on the basis of the model shown in Fig. 18.† Copper diffuses from the alloy to the

Table V. Rate Constants for the Oxidation at Cu-Pt and Ni-Pt Alloys

| Composition, Atomic Pct                    | T, °C | Atmosphere: O <sub>2</sub> at 1 atm pressure |                                    |                                                        |
|--------------------------------------------|-------|----------------------------------------------|------------------------------------|--------------------------------------------------------|
|                                            |       | $K_E$ ,<br>Cm <sup>2</sup> per Sec           | $K_S$ ,<br>Cm <sup>2</sup> per Sec | $K_m$ ,<br>Mg <sup>2</sup> per<br>Cm <sup>4</sup> -Sec |
| Cu-6.38%Pt                                 | 1000  | $1.22 \times 10^{-7}$                        | $1.51 \times 10^{-8}$              | $6.90 \times 10^{-2}$                                  |
|                                            | 925*  | $3.68 \times 10^{-8}$                        | $4.31 \times 10^{-9}$              | $1.90 \times 10^{-2}$                                  |
|                                            | 850*  | $1.55 \times 10^{-8}$                        | $2.08 \times 10^{-9}$              | $8.90 \times 10^{-3}$                                  |
| Cu-13.78%Pt                                | 1000  | $3.43 \times 10^{-8}$                        | $1.53 \times 10^{-8}$              | $1.74 \times 10^{-2}$                                  |
|                                            | 925   | $1.25 \times 10^{-8}$                        | $4.76 \times 10^{-9}$              | $5.73 \times 10^{-3}$                                  |
|                                            | 850*  | $6.25 \times 10^{-9}$                        | $2.50 \times 10^{-9}$              | $3.61 \times 10^{-3}$                                  |
| Cu-25.65%Pt                                | 1000* | $1.02 \times 10^{-8}$                        | $1.33 \times 10^{-8}$              | $6.78 \times 10^{-3}$                                  |
|                                            | 925*  | $4.65 \times 10^{-9}$                        | $4.61 \times 10^{-9}$              | $2.60 \times 10^{-3}$                                  |
|                                            | 850*  | $2.50 \times 10^{-9}$                        | $2.08 \times 10^{-9}$              | $1.81 \times 10^{-3}$                                  |
| Ni-15%Pt                                   | 1000  | $2.68 \times 10^{-10}$                       | $3.78 \times 10^{-10}$             | $6.40 \times 10^{-4}$                                  |
|                                            | 925   | $1.53 \times 10^{-10}$                       | $7.47 \times 10^{-11}$             | $2.08 \times 10^{-4}$                                  |
|                                            | 850   | $5.84 \times 10^{-11}$                       | $1.39 \times 10^{-11}$             | $8.61 \times 10^{-5}$                                  |
| Ni (avg)<br>(Kubaschewski<br>and Goldbeck) | 1000  | $2.60 \times 10^{-10}$                       |                                    | $6.61 \times 10^{-4}$                                  |
|                                            | 925   | $0.825 \times 10^{-10}$                      |                                    | $2.10 \times 10^{-4}$                                  |
|                                            | 850   | $2.48 \times 10^{-11}$                       |                                    | $6.3 \times 10^{-5}$                                   |

\* Negative deviation from parabolic behavior after 6 hr.

† For details on the derivation of the kinetic equations order Document 3336 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D.C., remitting \$1.00 for microfilm (images 1 in. high on standard 35 mm motion picture film) or \$1.00 for photocopies (6x8 in.) readable without optical aid.

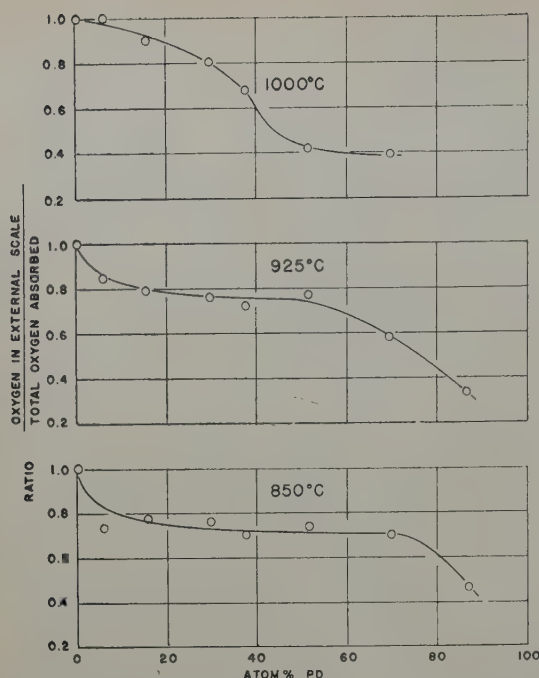


Fig. 16—Relative amount of oxygen in the external scale, Cu-Pd alloys.

alloy/subscale interface at which point the concentration is  $C_1$ . From the alloy/subscale interface to the subscale/scale interface, copper diffuses in the metal phase of the subscale as a result of the concentration gradient  $(C_1 - C_2)/S$ . Diffusion of copper in the external scale results from the concentration gradient  $(C_3 - C_4)/E$ . Reaction with oxygen takes place at the scale/oxygen interface, the thin layer of  $\text{CuO}$  being neglected. The subscale forms as a result of the inward diffusion of oxygen along the gradient  $(C_5 - C_6)/S$ , the oxygen having originated by dissociation of  $\text{Cu}_2\text{O}$  at the scale/subscale interface. It is convenient to use the initial gas/metal interface as the origin of the distance coordinate. Thus  $v$  is the thickness of metal oxidized to  $\text{Cu}_2\text{O}$  and  $p$  is the distance of the subscale/alloy interface from the initial surface. Although the model chosen involves the oxide  $\text{Cu}_2\text{O}$ , it is obvious that the result can be generalized. It is assumed that the concentration gradients in the scale and

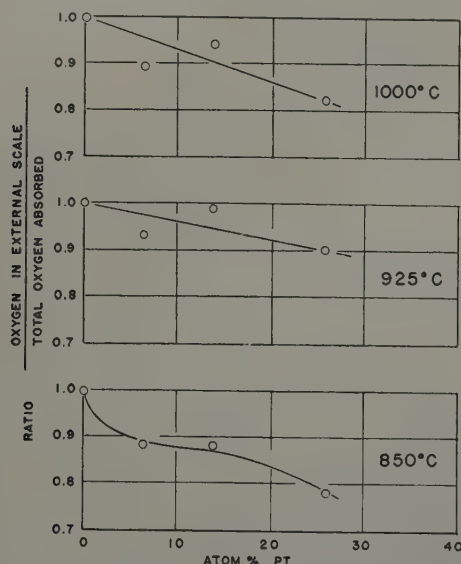


Fig. 17—Relative amount of oxygen in the external scale, Cu-Pt alloys.

subscale are linear, that the subscale oxide particles offer no barrier to diffusion, and that both scale and subscale grow parabolically according to eqs 2 and 3. The concentrations  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$ , and  $C_6$  are assumed independent of time for a given alloy and a given set of environmental conditions. A derivation based on Fick's law leads to the following equations:

$$\sqrt{K_E} = \frac{D(C_3 - C_4)}{\frac{\epsilon(C_5 - C_6)D_o}{\sqrt{K_E}} + \frac{C_2\sqrt{K_E}\delta}{2}} \quad [5]$$

$$\sqrt{\kappa} = \frac{2D(C_3 - C_4)}{\sqrt{K_E}(C_0 - C_1)} \frac{(1 - 2D_M)}{\kappa} \quad [6]$$

$$\sqrt{\kappa} = \delta\sqrt{K_E} + \sqrt{K_E} \quad [7]$$

where  $D$  is the diffusion coefficient for copper ions in  $\text{Cu}_2\text{O}$ ;  $D_M$ , the diffusion coefficient for copper in the alloy;  $D_o$ , the diffusion coefficient for oxygen in the metal phase of the subscale;  $\epsilon = 2$  atomic wt of copper divided by atomic wt of oxygen;  $\delta = \frac{Q_{\text{Cu}_2\text{O}} \cdot 2W_{\text{Cu}}}{Q_{\text{Cu}} \cdot W_{\text{Cu}_2\text{O}}}$ , in which  $Q$  is the density in g per cu cm and  $W$ , formula weight; and  $\kappa$  is defined by:  $p^2 = \kappa t$ . The concentration terms are as

Table VI. Calculated Values of the Parabolic Rate Constant,  $K_E$ , for Cu-Pd Alloys

| Composition,<br>Atomic<br>Pct Pd | $K_E \times 10^{-8}$ cm <sup>2</sup> per Sec |      |       |       |       |        |
|----------------------------------|----------------------------------------------|------|-------|-------|-------|--------|
|                                  | 1000°C                                       |      | 925°C |       | 850°C |        |
|                                  | Calc.                                        | Exp. | Calc. | Exp.  | Calc. | Exp.   |
| 5.19                             | 15.0                                         | 13.9 | 4.4   | 3.96  | 1.3   | 1.18   |
| 15.13                            | 7.8                                          | 7.10 | 2.4   | 2.12  | 1.0   | 0.885  |
| 29.65                            | 3.3                                          | 2.61 | 2.2   | 0.805 | 0.31  | 0.302  |
| 37.50                            | 0.84                                         | 0.88 | 0.55  | 0.264 | 0.11  | 0.0995 |

indicated in Fig. 18. Eq. 6 is subject to the restriction that  $\frac{\kappa}{2D_M}$  is large, otherwise the last term be-

comes more complex. If the concentration terms and diffusion coefficients were known it would be possible to solve eqs 5, 6, and 7 simultaneously for  $K_E$  and  $K_S$ . However, since some of the constants are not known it is necessary to treat eqs 5 and 6 separately. Since eq 5 is a quadratic in  $\sqrt{K_E}$  if  $K_S$  is taken as a known constant, it is possible to substitute values of the various terms as follows: The values of  $C_5$  and  $D_o$  are taken as the values for pure copper given by Rhines and Mathewson<sup>8</sup> and assumed independent of the alloy composition;  $C_6$  was assumed to be zero.  $C_2$  was measured for one alloy and calculated as a function of alloy composition using an independent equation which is due to Wagner.

$$\frac{K_E}{K_{E(\text{Cu})}} = \frac{1 - \sqrt{\frac{C_B}{C_2}}}{1 - \sqrt{C_B}} \quad [7]$$

where  $K_{E(\text{Cu})}$  is the parabolic rate constant for unalloyed copper;  $C_B$ , the mol fraction of the alloy phase in equilibrium with the oxide phase and an external oxygen pressure  $P_{\text{O}_2}^a$ .

The values of  $C_2$  obtained from this equation are shown in Fig. 19. The quantity  $D(C_3 - C_4)$  was calculated assuming that the quantity  $(C_3 - C_4)$  is pro-



portional to  $(C_2 - C_B)$  and that  $D$  is independent of the composition of the oxide. The term  $K_B$  was taken as a known constant, using the experimental values. The value of  $K_B$  so calculated from eq 5 are given in Table VI together with the experimental values. The agreement is quite good. While it is recognized that this agreement is in part due to the fact that experimental values of  $K_B$  and values of  $C_2$  calculated from  $K_B$  and  $K_S$  by means of an independent equation were employed, it is evident that eq 5 is valid. The relative magnitude of the various terms in eq 5 is such that the rate constant for the external scale is largely dependent upon diffusion of copper in the alloy. The fact that  $D_M$  does not appear explicitly in eq 5 is not significant, since its effect is exerted through the choice of  $C_2$  and  $K_B$ .

Eq 6 cannot be treated in the same way as eq 5 since the quantity  $C_1$  is not known. Under the circumstances all that can be done is to insert experimental values of  $\chi$  and  $K_B$ , calculate  $C_1$ , and judge whether the result is reasonable. The quantity  $D(C_3 - C_4)$  was calculated as for eq 5, and values of  $D_M$  were taken from the work of Thomas and Birch- enall<sup>9</sup> as follows:  $1.7 \times 10^{-10}$  cm<sup>2</sup> per sec at 1000°C,  $5.8 \times 10^{-11}$  cm<sup>2</sup> per sec at 925°C, and  $1.73 \times 10^{-11}$  cm<sup>2</sup> per

Table VII. Calculated Values of the Copper Concentration at the Alloy/Subscale Interface

| $C_0$ , Mol Fraction Cu | Temperature, °C | $C_1$ , Mol Fraction Cu | $C_2$ , Mol Fraction Cu | $C_B$ , Mol Fraction Cu |
|-------------------------|-----------------|-------------------------|-------------------------|-------------------------|
| 0.95                    | 1000            | 0.58                    | 0.61                    | 0.31                    |
| 0.85                    | 1000            | 0.65                    | 0.42                    | 0.31                    |
| 0.70                    | 1000            | 0.57                    | 0.35                    | 0.31                    |
| 0.63                    | 1000            | 0.57                    | 0.32                    | 0.31                    |
| 0.95                    | 925             | 0.61                    | 0.55                    | 0.31                    |
| 0.85                    | 925             | 0.65                    | 0.41                    | 0.31                    |
| 0.70                    | 925             | 0.33                    | 0.40                    | 0.31                    |
| 0.63                    | 925             | 0.47                    | 0.33                    | 0.31                    |
| 0.95                    | 850             | 0.74                    | 0.51                    | 0.34                    |
| 0.85                    | 850             | 0.64                    | 0.46                    | 0.34                    |
| 0.70                    | 850             | 0.57                    | 0.37                    | 0.34                    |
| 0.63                    | 850             | 0.54                    | 0.35                    | 0.34                    |

sec at 850°C, for mol fraction copper equal to 0.32. The calculated values of  $C_1$  are shown in Table VII in which it is seen that, with but two exceptions, the calculated values of  $C_1$  lie between  $C_0$  and  $C_2$  as they should. Furthermore, the metal at the alloy subscale interface in all specimens was observed to have no trace of copper color, hence  $C_1$  must be less than 0.80 mol fraction copper. The calculated values of  $C_1$  are less than this value. Eq 6 is presumed to be essentially correct inasmuch as it yields reasonable values of  $C_1$ .

It is appropriate to point out that the copper concentration gradient in the subscale is probably the limiting factor for the growth of the external scale, since  $S$  is generally comparatively large. If, as has been assumed, the subscale thickness is mainly determined by the amount of oxygen diffused from the scale/subscale interface, then the copper concentration gradient across the subscale is dependent upon it, and likewise the growth of the external scale. Thus the rate of growth of the external scale is limited more by the small copper concentration gradient in the subscale than by the copper concentration in the unoxidized alloy.

Eqs 5 and 6 have been applied above to the alloys which form  $\text{Cu}_2\text{O}$  in the scale and subscale. These equations could also be applied to the case in which the scale and subscale oxide are  $\text{CuO}$ . In this case the dependence of  $K_B$  upon the alloy composition

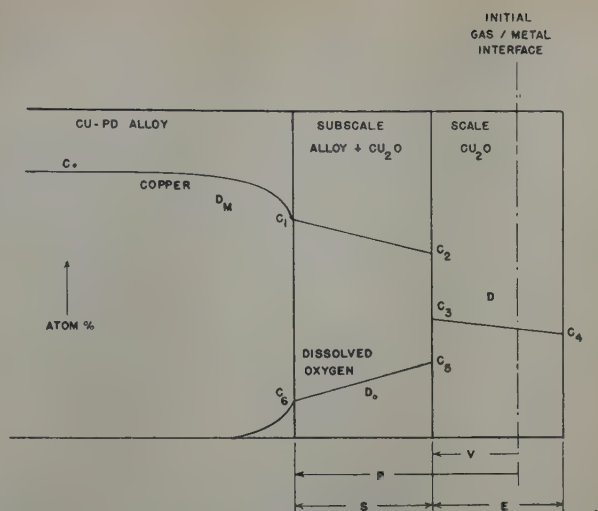


Fig. 18—Concentration gradients arising during the oxidation of a base metal-noble metal alloy as typified by the Cu-Pd alloys.

would be expected to be similar to that for the case in which only  $\text{Cu}_2\text{O}$  occurs. This is verified in Fig. 9. The transition from  $\text{Cu}_2\text{O}$  to  $\text{CuO}$  in the scale and subscale with increasing palladium content (decreasing  $C_0$ ) is pictured as follows. For the alloys high in copper, the stationary copper concentration  $C_2$  at the scale/subscale interface is maintained at a value greater than the equilibrium value,  $C_B$ . As  $C_0$  decreases, a place is reached where diffusion of copper to the scale/subscale interface can no longer maintain  $C_2$  greater than  $C_B$ . Then the scale becomes  $\text{CuO}$ , and  $C_2$  is less than  $C_B$ , but greater than  $C_B'$ , where  $C_B'$  is the copper concentration in equilibrium with  $\text{CuO}$ . When  $C_2$  is only slightly less than  $C_B$ , and  $C_1$  is greater than  $C_B$ , the external scale would be  $\text{CuO}$  and the subscale oxide  $\text{Cu}_2\text{O}$ . This is the transition case between the first case in which only  $\text{Cu}_2\text{O}$  is found and the second case in which only  $\text{CuO}$  is found. As  $C_0$  is further decreased, a point will be reached where  $C_2$  can no longer be main-

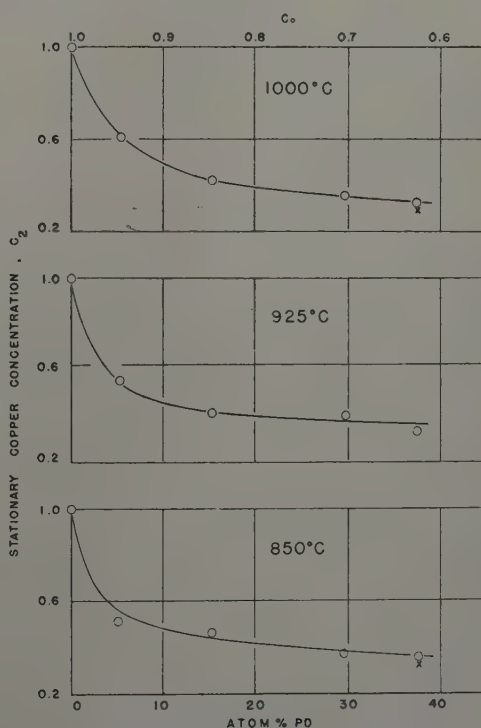


Fig. 19—Stationary Cu concentration at the scale/subscale interface, calculated. Cu-Pd alloys with  $\text{Cu}_2\text{O}$  scale. Experimental points represented by X.

tained at a value greater than  $C_s'$ . At this point the oxide (probably containing considerable copper) appears.

It is believed that the kinetic equations could be applied to other binary solid solution systems in which the affinity of the solvent toward oxygen is much greater than that of the solute. In this connection it is noted that platinum is more noble than palladium, and yet no fundamental difference is found between the oxidation of their alloys with copper. As a matter of fact, palladium appears to deviate sufficiently from nobility that the oxidation of Cu-Pd alloys may be considered as a connecting link between the ideal base metal-noble metal case and the base metal-base metal case of alloy oxidation.

The effect of the diffusion coefficient in the alloy upon the oxidation rate is shown by comparing the oxidation rates and diffusion rates for Cu-Pd and Cu-Pt alloys. This cannot be discussed quantitatively on the basis of eqs 5 and 6 since, in passing from one system to the other, the concentration terms for copper and oxygen, and the diffusion coefficient for oxygen in the metal change. Diffusion coefficients for the Cu-Pt system extrapolated from the data of Kubaschewski and Ebert<sup>10</sup> are from 0.03 to 0.05 times the corresponding values for the Cu-Pd alloys. It is to be expected then that the copper concentration  $C_1$ ,  $C_2$ , and  $C_3$ , would be smaller for the Cu-Pt alloys. This would, of course, result in a smaller rate of delivery of copper to the scale/oxygen interface, hence a smaller value of  $K_s$ . That this is the case may be seen in Fig. 12.

The temperature dependence of the rate constants  $K_s$  and  $K_{ss}$  is generally not of the Arrhenius type. There is no reason to expect an Arrhenius type dependence, because of the fact that the concentration terms in eqs 5 and 6 do not follow such a temperature dependence.

Wagner's theory for the oxidation of binary alloys containing one noble metal results in two equations, one of which (eq 7) has been used successfully here. This equation does not involve the diffusion coefficient for the alloy. The other equation involves the diffusion coefficient in the alloy and disregards subscale formation. The latter equation does not fit the experimental data.

### Conclusions

1—The oxidation of Cu-Pd and Cu-Pt alloys has been studied as a function of composition and temperature from the standpoint of the kinetics of scale and subscale growth and the structure and morphology of the reaction products. Under the conditions of the experiments a subscale is always formed beneath the external scale. Rate constants for the external scale thickness decrease regularly with increasing noble metal content in the alloy. Rate constants for the subscale thickness pass through a maximum which occurs at higher noble metal content the higher the temperature of oxidation for the Cu-Pd system, and which is independent of temperature for the Cu-Pt system. The rate constants generally do not follow a temperature dependence of the Arrhenius type.

2—The scale and subscale structure has been discussed in terms of a necessarily schematic equilibrium diagram for the two metals and oxygen.

3—The morphological features of the scale and subscale have been discussed. Chief among these is

the preferential precipitation of oxide at grain boundaries in the subscale.

4—In addition to previously published<sup>7</sup> criteria for subscale formation the further criterion that noble metal must go into solid solution in the base metal oxide must be considered in order to explain the formation of a subscale in alloys with noble metals.

5—Kinetic equations for the rate constants for the scale and subscale involving concentrations of the various diffusing elements and diffusion coefficients for the base metal and oxygen in the alloy, and the base metal in the oxide have been derived.

6—Calculations based on the kinetic equation for the external scale agree with the experimental data. Calculations based on the kinetic equation for the subscale yield reasonable results, but this equation must be considered less firmly established than that for the external scale.

7—The rate constant for the external scale is primarily governed by diffusion of the base metal through the subscale zone. The rate constant for the external scale and the diffusion coefficient in the metal phase are smaller for the Cu-Pt alloys than for the corresponding Cu-Pd alloys.

8—The rate constant for the subscale is largely determined by the inward diffusion of oxygen to the subscale/alloy interface.

9—The kinetic equations are believed to be applicable to the oxidation of solid solution alloys of a base metal and a metal considerably more noble.

10—One of the equations of Wagner appears to be applicable to the present case; the other leads to results not in agreement with experimental measurements.

11—A subscale was observed to form in a Ni-Pt alloy, but is less extensive than that found in the Cu-Pd and Cu-Pt alloys.

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# Plasticity of Molybdenum Single Crystals

by N. K. Chen and R. Maddin

In the extension of molybdenum single crystals at room temperature, the slip planes were found to be of the type  $\{110\}$ ; the slip direction  $\langle 111 \rangle$ . Theories of plasticity of body-centered cubic metals have been examined, and an explanation based upon planes of highest atomic density seems plausible to explain the plastic behavior of molybdenum single crystals.

IN body-centered cubic metals, slip has been reported to occur on several planes; these are of the type  $\{110\}$ ,  $\{112\}$ , and  $\{123\}$ . Andrade has correlated<sup>1</sup> the operative slip planes in body-centered cubic metals with the testing temperature relative to the melting point. In this correlation, if  $T$  is the absolute temperature at which slip takes place and  $T_m$  the absolute melting point, then the acting slip planes in body-centered cubic metals may be arranged as shown in Table I. However, deviations from this correlation have been reported in iron and iron-silicon alloys<sup>2</sup> and also in molybdenum deformed at a temperature around 2400°C.<sup>3</sup>

In the case of iron and other body-centered cubic metals or alloys in which all three slip planes have been reported to be active at any one temperature, the crystallographic mechanism of slip is not well understood. Numerous investigators in this field have assumed that the resolved shear stress is a deciding factor. Such considerations were given by Gough in his experiments with repeated torsion of iron single crystals<sup>4</sup> and recently by Opinsky and Smoluchowski in their study of iron-silicon alloys,<sup>5</sup> and will be dealt with later in this report.

A third possibility is that slip lines in body-centered cubic metals may be formed by alternate slip on nonparallel  $\{110\}$  planes and not by slip on any plane of higher indices. This was advanced by Elam in the case of  $\beta$  brass.<sup>6</sup> Since  $\{110\}$  planes are planes of highest atomic density in the body-centered cubic structure, this hypothesis would be in accordance with the plastic behavior of metals in other systems, namely, face-centered cubic and hexagonal close-packed. Experimental evidence in support of this hypothesis is lacking. Nevertheless the work of Barrett, Ansel, and Mehl<sup>7</sup> has definitely

Table I. Arrangement of Acting Slip Planes in Body-Centered Cubic Metals

| Metals                | $T/T_m$   | Slip Plane |
|-----------------------|-----------|------------|
| W, Mo, Na             | 0.08-0.24 | $\{112\}$  |
| Mo, Na, $\beta$ brass | 0.26-0.50 | $\{110\}$  |
| Na, K                 | 0.80      | $\{123\}$  |

demonstrated that the slip resistance on  $\{110\}$  planes in iron is very much smaller compared with that on  $\{112\}$  and  $\{123\}$  planes.

In the present investigation, molybdenum single crystals were carefully documented as to the operative slip planes and lattice reorientations after plastic extension at room temperature. In three crystals studied,  $\{110\}$  planes were found to be active invariably rather than the  $\{112\}$  planes, which were previously reported for molybdenum at this temperature<sup>7</sup> and predicted by Andrade's theory.<sup>1</sup>

In two other cases  $\{112\}$  and  $\{123\}$  planes seemed to operate together with  $\{110\}$  planes as active slip planes. However, it is believed, after careful analysis of crystallite and lattice rotations, that slip on  $\{112\}$  and  $\{123\}$  planes may be spurious. Particular reference will be made to the formation of asterism, lattice rotation, and crystallite rotation in an attempt to show that slip apparently observed on  $\{112\}$  and  $\{123\}$  planes is actually slip on nonparallel  $\{110\}$  planes.

## Materials and Treatment

Sintered molybdenum rods  $\frac{1}{8}$  in. in diam, obtained from the Fansteel Metallurgical Co., were reported to have a purity of 99.9 pct.\* One specimen, Mo-13,  $\frac{1}{4}$  in. in diam, was supplied by Westinghouse Electric Corp.

Single crystals were prepared, using the technique devised by Chen, Maddin, and Pond.<sup>8</sup> Mo-13 was  $\frac{1}{4}$  in. in diam x 7 in. long with a reduced gage section of 0.200 in. in diam x 3 in. long. The center of

\* C 0.001  $\pm$  0.001 pct (as-received).

C 0.003  $\pm$  0.001 pct single crystal (Battelle Memorial Institute).

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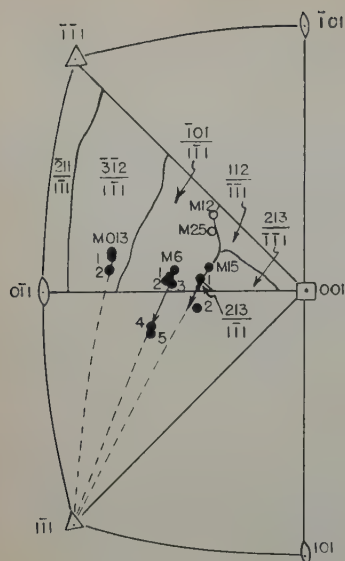


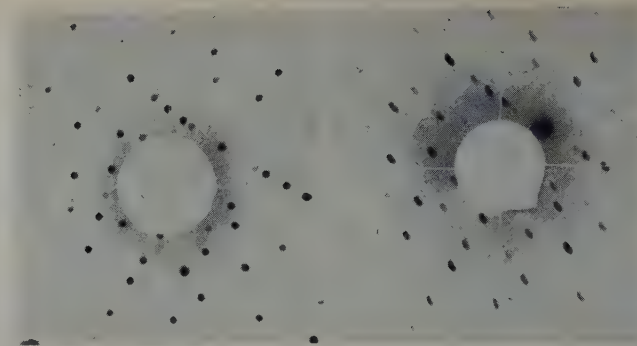
Fig. 1—Orientations of crystals investigated.

The orientations of Mo-13 and M-15 after the first and second extension, and of M-6 after the first, second, third, fourth, and fifth extension are included.

the gage section contained a single crystal  $1\frac{1}{4}$  in. in length. All other specimens, M-6, M-15, M-25, and M-12, were  $\frac{1}{8}$  in. in diam x 7 in. long, with single crystals approximately 2 to 3 in. in length occupying the entire center sections of each specimen. All specimens were electrolytically polished, using an electrolyte of 300 cc methyl alcohol, 60 cc  $H_2SO_4$ , 130 cc HCl, and a current density of 4 amperes per sq in. The specimens were pulled in a Tinius-Olsen beam-type testing machine using SR-4 type A-8 strain gages and strain indicator. Load values were estimated to within 1 lb. The orientation of each specimen was determined before and after each extension by using an X-ray back-reflection Laue method.

### Determination of Slip Elements

The orientations of all the crystals are shown in Fig. 1 in a standard cubic stereographic projection. The movements of the stress axes for Mo-13, M-6, and M-15 after various extensions, are indicated by the shift in the stress axis to position 1, 2, etc., respectively. The axis shift clearly shows a rotation toward the direction  $[\bar{1}\bar{1}1]$ , which is the slip direction in these three crystals. It was noted that both M-6 and M-15 rotated toward the  $[\bar{1}\bar{1}1]$  direction



a—Before extension.                      b—After extension to yield.

even when the symmetry curve, represented by the line joining (001) and  $(0\bar{1}1)$ , was reached by the stress axes. This may be due to an insufficient amount of slip on the conjugate slip plane, (101), so that the path of stress-axis rotation did not revert toward the direction  $[\bar{1}\bar{1}1]$ . Microscopic examination showed that the second slip system, (101), was not prominent even at the end of the fourth extension of M-6 and the last extension of M-15 (cf. Fig. 5b and c).

Crystals M-25 and M-12 behaved differently from those mentioned above. Their behaviors will be analyzed separately in the following sections.

At the early stage of deformation, the slip lines were quite straight and uniformly dispersed, though very faint, resembling striations. An alteration of the Laue spots, indicating the initial stage of "asterism," was invariably observed in all specimens when they were extended to just beyond their yield. A set of typical photograms from Mo-13 before and after extension is shown in Fig. 2a and b. Slip lines were very difficult to observe at the yield because of the fineness of the lines, whereas a decided change in the Laue reflection could easily be noted (cf. Fig. 2b). In correlating slip traces measured on the metallograph with the orientation determined from X-ray, the orientation of the specimens after deformation was always used.

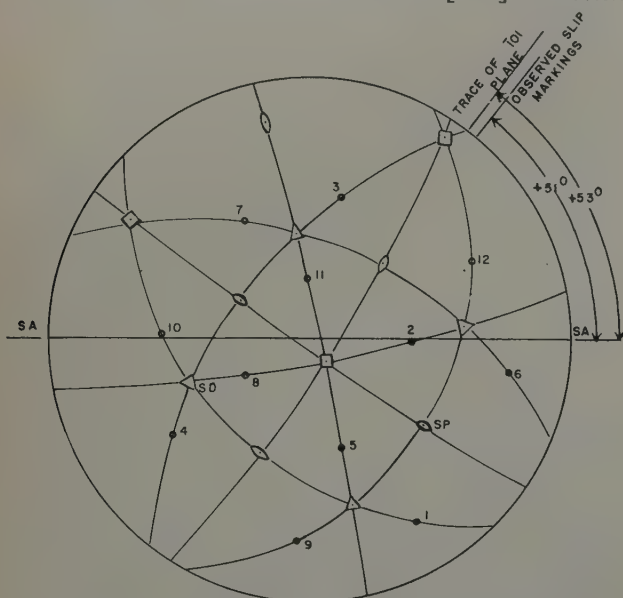


Fig. 3—Projection showing orientation of Mo-13. Specimen axis SA, horizontal. SP and SD represent the observed slip plane and slip direction; 1 to 12 represent the 12  $\{112\}$  planes.

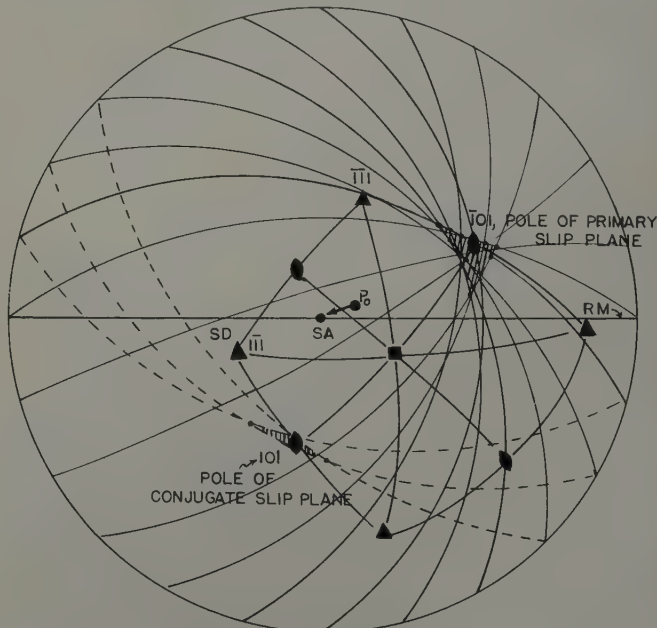


Fig. 4—Determination of the pole of the slip traces, M-6. Stress axis SA, at the center of projection, and X-ray beam containing the reference mark RM is perpendicular to stress axis.  $P_0$  is the initial orientation. Errors measured from  $(\bar{1}01)$  pole to each individual determination is  $0^\circ$  to  $6^\circ$ .



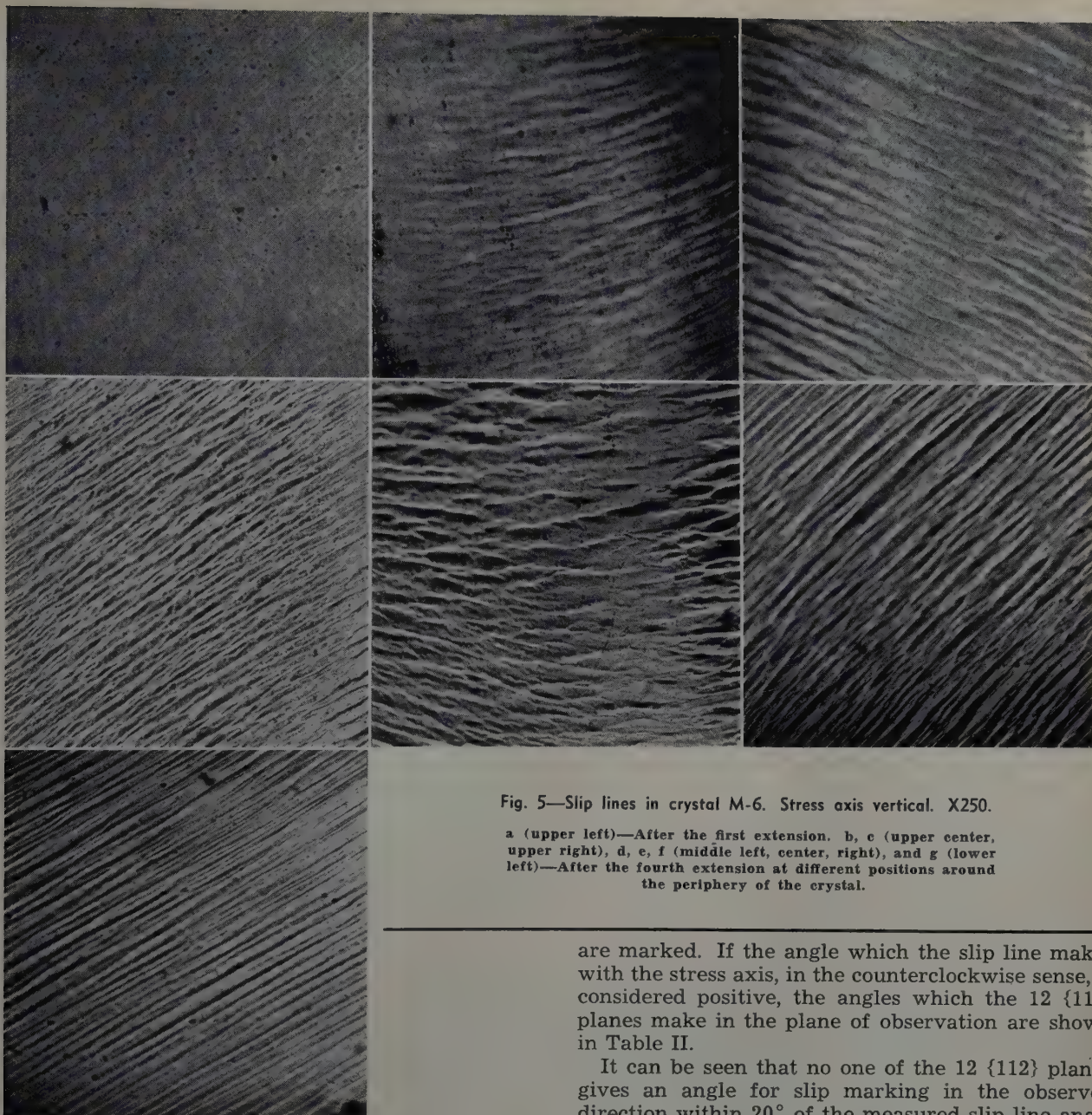


Fig. 5—Slip lines in crystal M-6. Stress axis vertical. X250.

a (upper left)—After the first extension. b, c (upper center, upper right), d, e, f (middle left, center, right), and g (lower left)—After the fourth extension at different positions around the periphery of the crystal.

It was found in three specimens, Mo-13, M-6, and M-15, that the  $(\bar{1}01)$  plane, the plane of highest resolved shear stress, was responsible for the observed slip markings, rather than any of the  $\{112\}$  planes as previously reported.<sup>7</sup> This was carefully checked and can be illustrated with the aid of Fig. 3 (specimen Mo-13), which shows, in projection, one plane of observation in which all 12 possible  $\{112\}$  planes

are marked. If the angle which the slip line makes with the stress axis, in the counterclockwise sense, is considered positive, the angles which the 12  $\{112\}$  planes make in the plane of observation are shown in Table II.

It can be seen that no one of the 12  $\{112\}$  planes gives an angle for slip marking in the observed direction within  $20^\circ$  of the measured slip line angle ( $51^\circ$  positive). Similar analyses were carried out in other planes of observation and the  $(\bar{1}01)$  plane was invariably obtained as the active plane of slip.

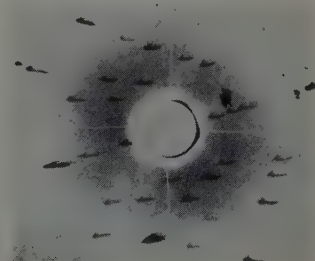
In the case of M-6, measurements were made at each  $15^\circ$  around the specimen axis on the metallograph. An indicator was attached to the specimen along a reference mark that was also used for the orientation determination by X-rays. The angle of rotation was measured on a protractor attached to the stage of the metallograph as given by the indicator. The angle between the specimen axis and the slip marking was measured on the metallograph at a magnification of X250. Thus, by plotting stereo-

Table II. Angles of  $\{112\}$  Planes in the Plane of Observation

| Planes $\{112\}$ | Angle, Degrees |          |
|------------------|----------------|----------|
|                  | Positive       | Negative |
| 1                | 21             |          |
| 2                | 88             |          |
| 3                |                | 12       |
| 4                |                | 54       |
| 5                | 16             |          |
| 6                | 78             |          |
| 7                | 29             |          |
| 8                |                | 60       |
| 9                |                | 3        |
| 10               | 88             |          |
| 11               | 2              |          |
| 12               |                | 64       |

Fig. 6—Laue photograph of crystal M-6 after the fourth extension.

X-ray beam perpendicular to plane containing specimen axis and minor elliptical axis.





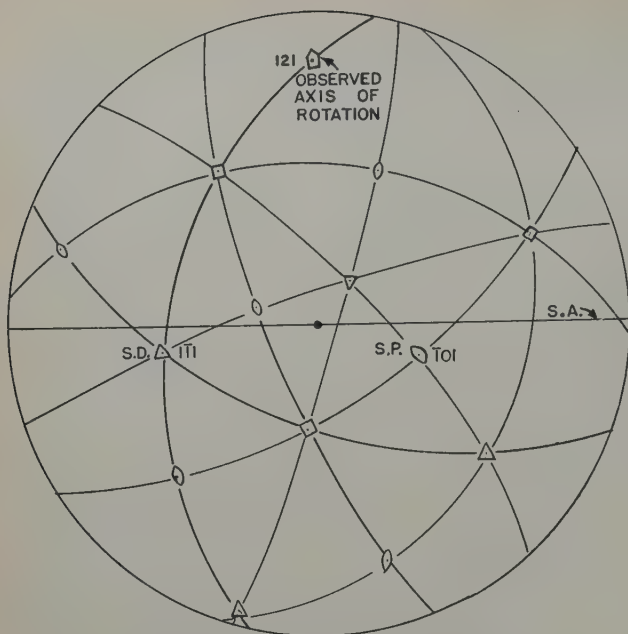


Fig. 7—Stereographic plot of asterism shown in Fig. 6.

graphically the pole representing the slip traces on each plane of observation, the position of the pole of the slip plane could be directly located at the intersections. For M-6, it was a small region, again clustered around the  $(101)$  pole, which is predicted as the plane having the highest resolved shear stress, Fig. 4. Fig. 5a to g represents the appearance of slip markings at different positions around the crystal. It should be noted that lines at the head of the glide ellipse are wavy in character, but those at a position approximately parallel to the slip direction are fairly straight. Conjugate slip lines could be witnessed in some areas as shown in Fig. 5b and c. They were determined to be  $(101)$  planes.

To check the crystallographic location of slip

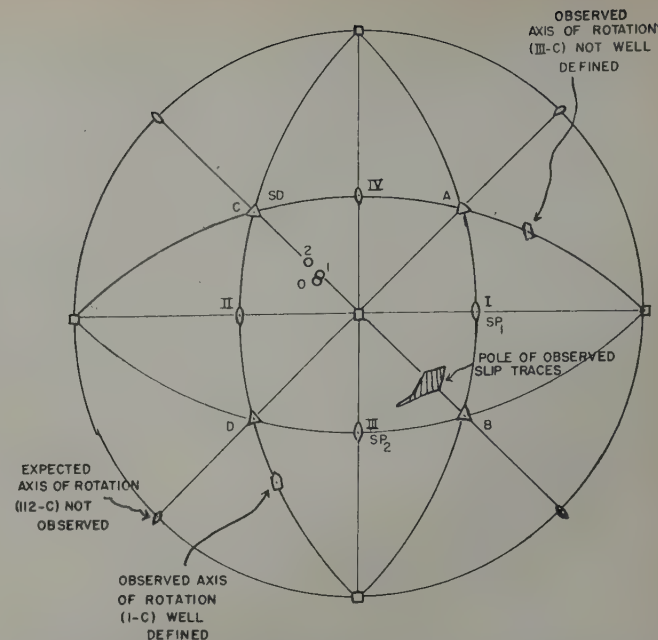


Fig. 8—Projection of M-12 showing the pole of observed slip traces, the axes of rotation determined from asterism, and the stress axis movement.

planes in M-6, an X-ray photogram was taken with the beam adjusted perpendicular to the plane containing the specimen axis and the minor elliptical axis. Fig. 6 indicates such a photogram having pronounced asterism. On plotting stereographically (Fig. 7), it is clearly seen that  $(101)$  plane should be the operative slip plane and  $[111]$  the slip direction, in order to account for the crystallite rotations occurring about the observed axis  $[121]$ , which is in the slip plane and  $90^\circ$  from the slip direction. This type of crystallite rotation has been reported in the deformation of many metal single crystals.<sup>9</sup>

The pole of observed slip traces in M-12, as

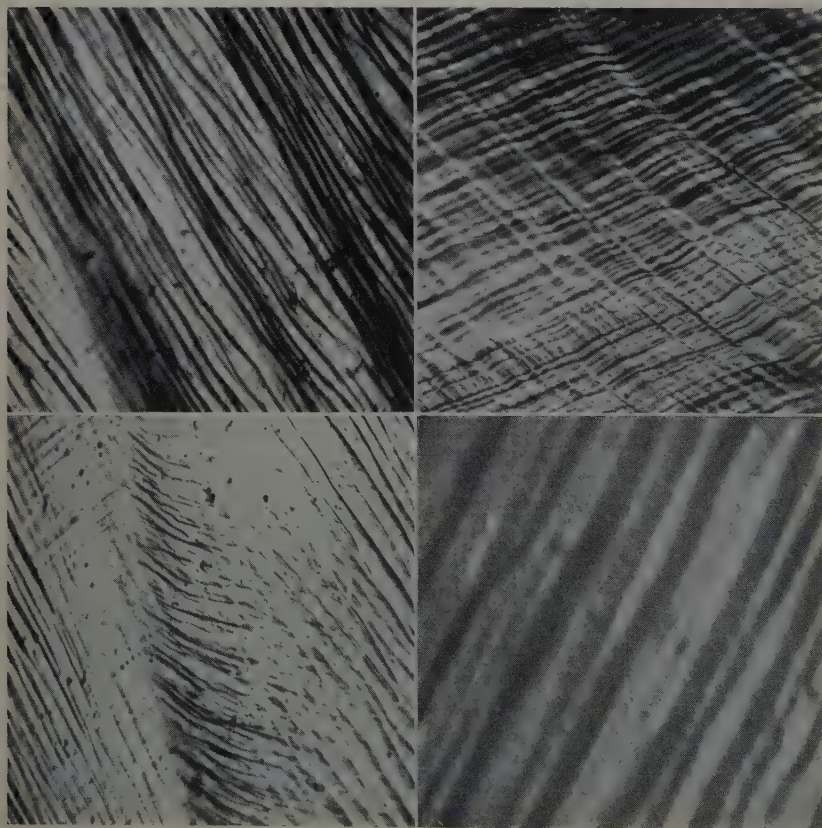


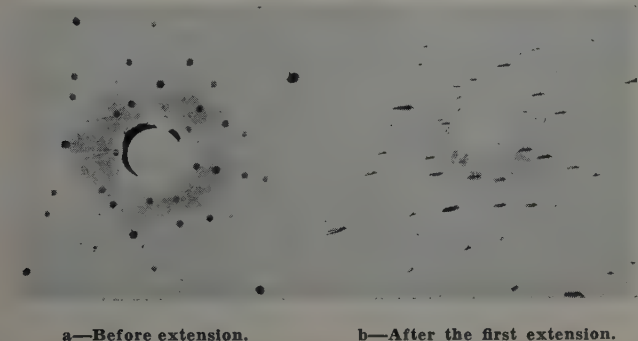
Fig. 9—Slip lines in M-12 after extension to shear failure.

a, b, c (upper left, upper right, lower left)—X500. d (lower right)—X2000.



determined by the optical method after the first extension, was very close to (112) as shown in Fig. 8. After the second extension, the specimen failed in a ductile manner, and the stress axis moved to the position 2 toward the  $[\bar{1}\bar{1}1]$  direction. The traces of a second system, which could be viewed only at a few locations, when plotted stereographically, appeared to be due to slip on the (011) plane. The participation of this plane was very slight and was difficult to observe. Representative micrographs of the slip lines are shown in Fig. 9a to d.

The observed location of slip traces shown in Fig. 8 after the first extension was checked by the X-ray method and analyzed according to the same technique used in Fig. 7. However, as indicated in Fig. 8, the expected axis of rotation in the plane (112) and  $90^\circ$  from the slip direction C was not observed. Instead, there appeared a well-defined axis of rotation which could be described only if the slip plane was (011) and the slip direction  $[\bar{1}\bar{1}1]$ , I-C in Fig. 8. This result appears more rigorous when the asterism in Fig. 10b is plotted stereographically. (Fig. 10a shows the initial orientation.) Careful examination indicated that the main asterism (Fig. 10b) in the approximately horizontal direction could be viewed as composed of at least two parts as shown enlarged in Fig. 10c. They seemed to represent rotations



a—Before extension.

b—After the first extension.



c—Enlargement of Laue spots in b.  
Fig. 10—Laue photograms of M-12.

about I-C and III-C, respectively (Fig. 8). Thus it is quite probable that the slip traces observed apparently on (112) planes were in reality slip on two {110} planes with a common slip direction.

The results for specimen M-25 are shown in Fig. 11. Here, again, the slip traces observed on the metallograph are shown plotted stereographically as areas in Fig. 11 clustering in the vicinity of the (123) pole. In addition, an area as determined from a second set of slip traces is shown clustering near the (011) pole. Based upon the slip traces as determined from metallographic observation, it would be said that the specimen had slipped on (011) and (123) [and/or (112)] planes. However, lattice and crystallite rotations shown in the photograms of Fig. 12a and b indicate, when plotted stereographically, that the planes of slip are actually (011) and (011); the slip systems being I-C and II-A respectively in Fig.

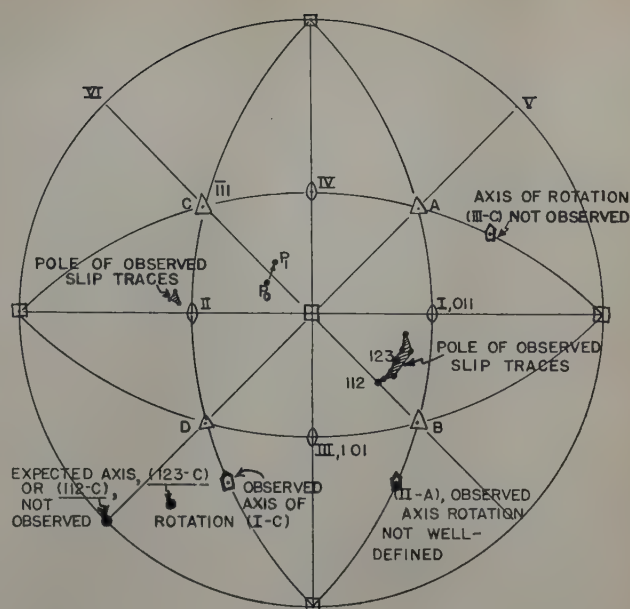
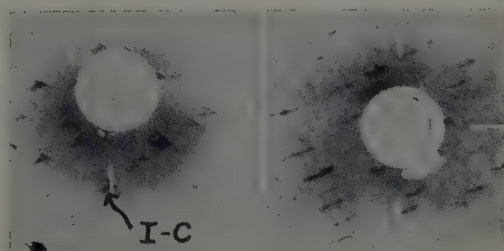


Fig. 11—Projection of M-25 showing the pole of the observed slip traces, the axis of rotation determined from asterism, and the stress axis movement.

11. It is difficult to explain the movement of the stress axis  $P_0$  to  $P_1$ , if slip had occurred only on (123)  $[\bar{1}\bar{1}1]$  (and/or (112)  $[\bar{1}\bar{1}1]$ ). If, however, slip had occurred on systems I-C and II-A, as indicated, the movement  $P_0$  to  $P_1$  could be rationalized by resolving it into two components moving towards A and C respectively.

In order to check carefully whether the asterism from which the crystallite rotations were determined was characteristic of the entire specimen or was indicative only of localized areas, a series of X-ray photograms was made at various positions along the specimen axis and around the periphery of the crystal. It was found that the asterism characteristic of one position was the same when a photogram was made  $180^\circ$  opposite to the first position.<sup>†</sup> In addition to the asterisms from which were determined the slip systems I-A and II-C, a third type was observed in a photogram which was taken  $63^\circ$  in azimuth from the reference mark (Fig. 12b). In an attempt to check the crystallite rotation at this position with the rotations previously determined, it was noted that the pronounced asterism in this position could only be accounted for by a rotation about the pole of the slip plane I (Fig. 13). From this it must be realized that a number of photograms must be made around the periphery of the specimen in order to detect the different lattice rotations involved in the deformation of the specimen. This is so, because at certain positions the distortions of the Laue spots indicative of different types of rotation may be superimposed on each other. Conse-



a—Plotted in Fig. 11.

b—Plotted in Fig. 13.

Fig. 12—Laue photograms taken at different positions around M-25 after extension.

<sup>†</sup> This indicates that the asterism is crystallographic in nature and represents a true account of plasticity in the specimen.

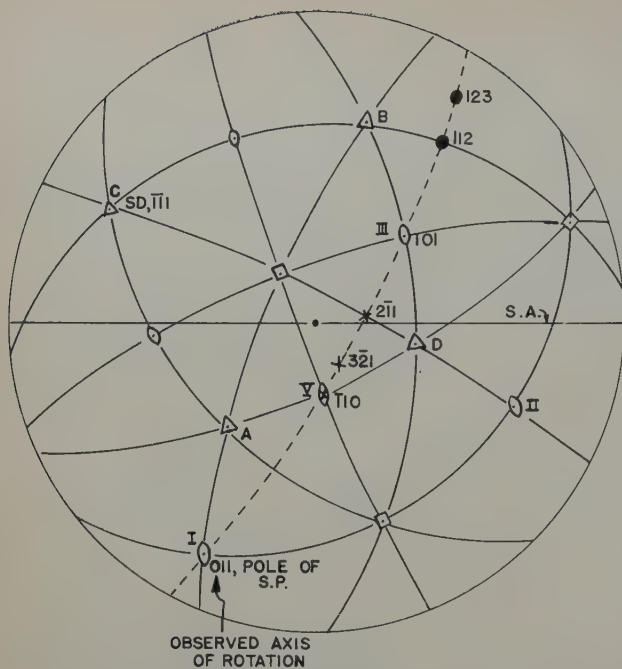


Fig. 13—Plot of asterism shown in Fig. 12b.

quently, the analysis at these positions becomes difficult.

At the head of the glide ellipse, the wavy character of the slip traces could be resolved into a series of saw-toothed markings. At a position away from the head, slip lines appeared to be clustered. The general direction of the cluster was used for the determination of the slip plane (see Fig. 11). However, when the fine lines of the cluster were plotted, they proved to be near a (011) pole.

### Stress-Strain Data

No attempt has been made to resolve the critical

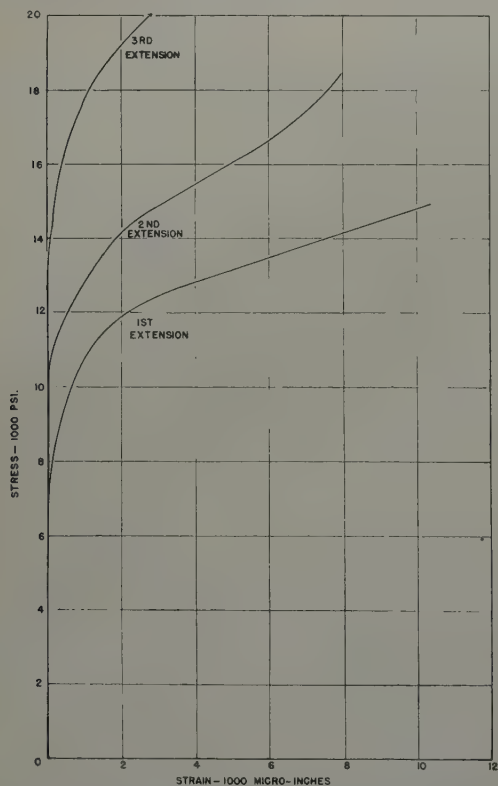


Fig. 14a—Stress-strain curves for M-6 after the first, second, and third extension.

shear stress, since, in specimens Mo-13, M-6, and M-15, the plane acting was the one of highest resolved shear stress, i.e.  $(\bar{1}01)$   $[\bar{1}11]$ ; but in specimens M-12 and M-25, there was more than one system acting. The stress-strain curves for the first, second, and third extensions are shown in Fig. 14a. The modulus of elasticity,  $E$ , was determined to be about  $20 \times 10^6$  psi for these curves. A plot of stress at yield vs. elongation is shown in Fig. 14b.

Specimen M-12 failed during the second extension with a typical ductile fracture as may be seen in Fig. 15a and b. The elongation at fracture was about 65 pct.

### Discussion

In view of the results reported herein, it is difficult to explain the behavior of molybdenum single crystals on the basis of Andrade's theory. His theory would predict that slip in molybdenum at room temperature would occur on  $\{112\}$  planes. Although Tsien and Chow<sup>7</sup> reported slip in molybdenum single crystals at room temperature on the  $\{112\}$  planes, only one crystal was investigated; whereas in the present work five specimens are shown to slip on  $\{110\}$ . Moreover, more than one method was used to determine the slip elements in the present work. It is realized that the work of Tsien and Chow involved the extension of molybdenum single crystals 0.25 mm in diam, whereas the present work used  $\frac{1}{8}$  and  $\frac{1}{4}$  in. specimens. It may be that the disagreement between their work and the present work is due to the difference of specimen size. It is contemplated to investigate molybdenum single crystals of very small size in the near future.

A number of investigators<sup>4-5</sup> have attempted to explain the activity of the slip elements on the basis of systems of highest resolved shear stress. For example, Opinsky and Smoluchowski<sup>5</sup> have computed mathematically the areas for systems,  $\{110\}$ ,  $\{112\}$ ,

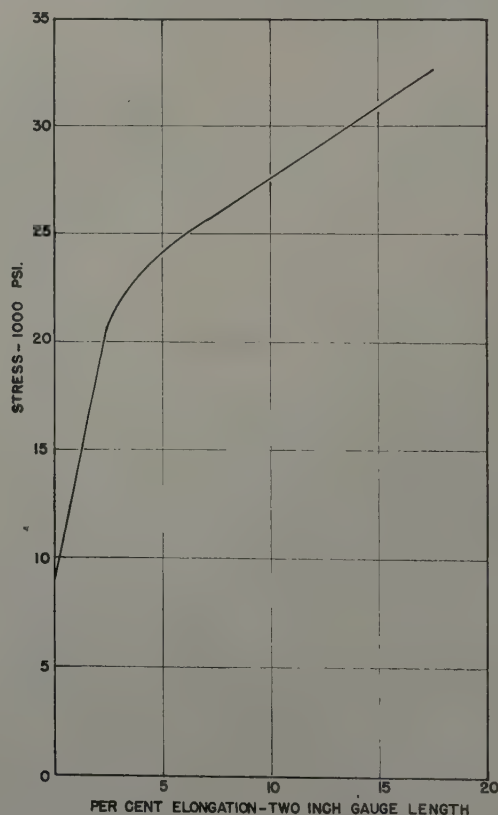


Fig. 14b—Stress at yield vs. elongation (strain-hardening curve).



and  $\{123\}$  in the direction  $\langle 111 \rangle$ , which have the highest resolved shear stress. In Fig. 16 there is shown a stereographic projection containing the areas of highest resolved shear stress with reference to the three types of planes reported to be active in the plasticity of body-centered cubic metals all in the  $\langle 111 \rangle$  direction. This plot was determined by measuring the  $\chi$  and  $\lambda$  values, where  $\chi$  is the angle between the slip plane and stress axis and  $\lambda$  is the angle between the slip direction and stress axis, for 94 different orientations covering the unit triangle. The plot is essentially in agreement with that produced by Opinsky and Smoluchowski. The Wulff net used here had an accuracy of  $\frac{1}{4}^\circ$ , and, thus, the boundaries shown in Fig. 16 are within an accuracy of  $\frac{1}{2}^\circ$ . It may be seen from Fig. 1, that specimen Mo-13 falls within the area devoted entirely to  $(\bar{3}\bar{1}2)$  slip, yet the observed slip plane was conclusively  $(\bar{1}01)$ . In the specimens M-12 and M-25 the  $(\bar{1}01)$ , the plane of highest resolved shear stress, was not observed.

M-15 should slip on both  $(\bar{1}01)$  and  $(213)$ , yet slip was found to occur only on  $(\bar{1}01)$ . Furthermore using the data on silicon-ferrite obtained by Opinsky and Smoluchowski,<sup>6</sup> it may be seen, Fig. 17, that there are many cases of disagreement with the predicted slip plane based upon highest resolved shear stress. This, of course, may be explained on the basis that the slip resistance on the three planes is not equal, as stated by Opinsky and Smoluchowski.



Fig. 15—Two views of shear failure in M-12. X2.

If, however, their explanation is valid, it must take into account the behavior of M-25 and M-12.

In the case of M-25, observation of the slip traces appeared to indicate that slip had occurred on the planes  $(123) [\bar{1}\bar{1}1]$  and  $(0\bar{1}1) [\bar{1}\bar{1}1]$ . The resolved shear stress on both these systems was calculated,

and the ratio of these stresses is  $\frac{(123) [\bar{1}\bar{1}1]}{(0\bar{1}1) [\bar{1}\bar{1}1]} = 1.07$ .

Again for M-12, the observation of slip traces appeared to indicate that slip had occurred on the plane  $(112) [\bar{1}\bar{1}1]$  and  $(0\bar{1}1) [\bar{1}\bar{1}1]$ . The resolved shear stress on both these systems was calculated,

and the ratio of these stresses is  $\frac{(112) [\bar{1}\bar{1}1]}{(0\bar{1}1) [\bar{1}\bar{1}1]} = 1.06$ .

However, the participation of the plane  $(0\bar{1}1)$  in both crystals appeared to be very slight, and the plane  $(\bar{1}01)$  is not observed. For a valid comparison,

the ratio  $\frac{(123) [\bar{1}\bar{1}1]}{(0\bar{1}1) [\bar{1}\bar{1}1]}$  would have to be measured,

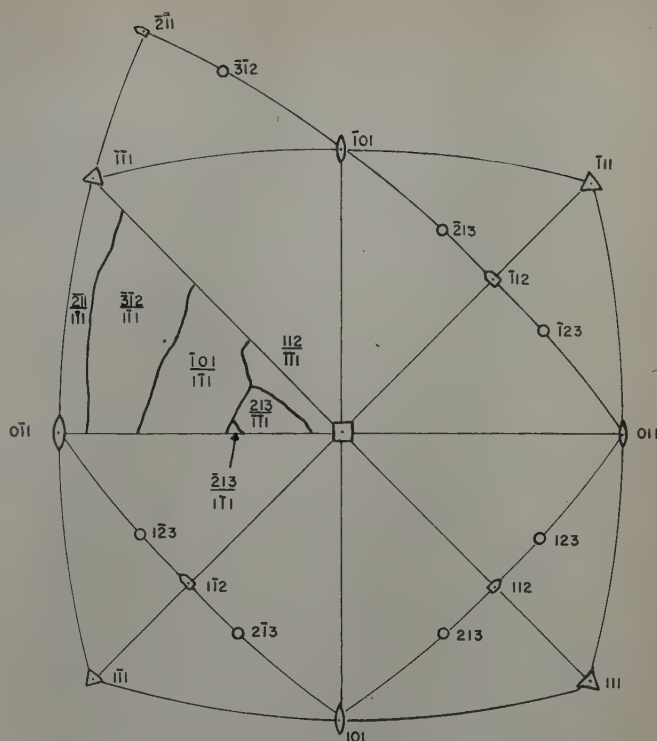


Fig. 16—Areas of highest resolved shear stress in the body-centered cubic lattice considering  $\{110\}$ ,  $\{112\}$ , and  $\{123\}$  planes in direction  $\langle 111 \rangle$ .

for the case of M-25 the ratio  $\frac{(112) [\bar{1}\bar{1}1]}{(0\bar{1}1) [\bar{1}\bar{1}1]}$  would

have to be measured, rather than the ratio  $\frac{(112) [\bar{1}\bar{1}1]}{(\bar{1}01) [\bar{1}\bar{1}1]}$ , as shown in Fig. 1 for this boundary.

Consequently, it would seem very difficult to document the activity of two types of planes, unless they are the correct ones and are operating simultaneously at the yield of the specimen with no lattice rotations involved.

A possible explanation for the operating slip systems may be based upon a consideration of the plane of the highest atomic density. It is to be noted that in face-centered cubic and hexagonal close-packed metals, the plane of maximum atomic density is always the one to operate. In the body-centered cubic metals, the plane of highest atomic density is  $\{110\}$  and of successively decreasing atomic density,  $\{001\}$ ,  $\{112\}$ ,  $\{111\}$ , and  $\{123\}$ . Since the direction  $\langle 111 \rangle$  is seldom in question as the

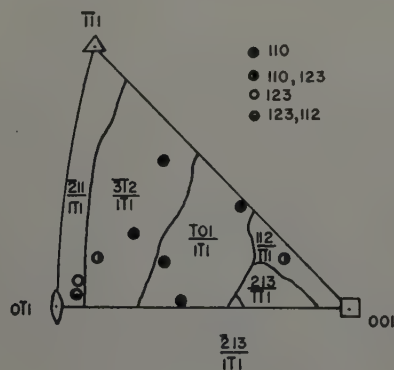


Fig. 17—Plot of data from Opinsky and Smoluchowski<sup>6</sup> within areas of highest resolved shear stress.

slip direction, the {001} and {111} planes can be discounted, since they do not contain this direction.

In the present investigation, the highest atomic density theory can be used conclusively to explain the behavior of Mo-13, M-6, and M-15, although there may be some doubt for M-12 and M-25 if only the optical data are considered. However, a number of pertinent facts must be considered before slip can be said to have occurred on low atomic density planes. For example, when the pole of the slip plane is obtained by the intersection of only two traces, there can be no scatter to the observed pole, despite the fact that the slip traces in body-centered cubic metals are inherently wavy. When the pole of the slip plane is obtained by plotting many traces, an area results. If this area falls in the vicinity of {112} pole, then that plane is reported as the plane of slip (cf. Fig. 8). If the area falls in the region of {123}, then this pole is generally reported to be the plane of slip (cf. Fig. 11). All of the past data have been reported generally with the understanding that measurements of the direction of wavy slip lines involve considerable error. Despite the fact that the microscopic appearance of slip traces must have represented the movement of atomic planes, these traces usually cannot be resolved with the optical microscope and hence may represent the integrated effect of more than one slip plane. It is suspected that the behavior of two nonparallel {110} planes would not present an integrated {110} trace; but might, under certain conditions, represent a {112} trace or a {123}. For example, if one of the two active {110} planes is predominant, the resulting trace could be {112}.

In the determination of slip elements, it seems more conclusive to consider the alterations in the structure as evidenced by the formation of asterism as a result of plastic deformation. It is to be expected that asterism would more nearly represent the structural changes occurring during deformation and would be a more sensitive indication, since it need not represent a grossly integrated condition as may be the case with the observation of slip traces.

In the present investigation, stereographic analysis of the asterism yields highly reproducible results. Invariably the axis about which rotation has taken place to produce the asterism is in a {110} plane. This points strongly to the condition that slip has occurred on planes of the type {110}, since the rotation of the slip plane toward the stress axis is about an axis in the slip plane and generally at right angles to the slip direction. The rotation axes determined in this manner were at right angles to  $\langle 111 \rangle$  directions.

It is interesting to note that Greninger stated in discussion to the paper by Barrett, Ansel, and Mehl that:<sup>2</sup>

"Is it not possible that traces corresponding approximately with {112} or {123} are really composites of alternate slipping on two or more {110} planes? All of these planes contain  $\langle 111 \rangle$  directions, and each {112} plane bisects the angle between {110} planes; likewise each {123} plane is located between a {110} and a {112} plane. Thus if slip were to proceed by approximately equal minute displacements along both  $(1\bar{1}0)$  and  $(01\bar{1})$ , the 'slip line' might appear as an approximate  $\{121\}$  trace; if the relative displacements were 4:1 (instead of being equal) the 'slip line' would be approximately  $\{2\bar{3}1\}$ ."

Recently Gouzou<sup>10</sup> stated that the success of the hypothesis that body-centered cubic metals slip uniquely on {110}  $\langle 111 \rangle$  systems appears to favor

the conclusion that slip on less densely populated planes is spurious and is actually duplex slip on {110}  $\langle 111 \rangle$  slip systems.

It is not completely understood at the present time why specimens Mo-13, M-6, M-15 show the active slip planes to be {110} unequivocally, both from the analysis of slip lines and asterism, whereas M-12 and M-25 behaved differently. It may be that the influence of orientation, on the distribution of shear stress, produces a change in distribution so as to affect the rotations of the slip planes and hence the character of slip traces.

It seems important to study carefully the formation and character of the slip lines with increasing deformation and as a function of orientation. It is contemplated to continue the work along this approach and to include careful investigations of other materials such as tungsten, niobium, and tantalum in an attempt to determine the parameters of plasticity of body-centered cubic metals.

### Conclusions

1—It has been found that molybdenum single crystals slip on the planes {110} in the direction  $\langle 111 \rangle$  for the specimens investigated to date.

2—An explanation for the participation of slip systems based upon temperature is held not tenable, at least in the case of molybdenum.

3—An explanation based upon systems of highest resolved shear stress does not appear to be conclusive, since, in the present work and others cited, cases of disagreement are observed.

4—An explanation based upon planes of highest atomic density, i.e., {110}, seems plausible to explain in part the plastic behavior of molybdenum single crystals.

### Acknowledgment

The authors would like to take this opportunity to thank the Battelle Memorial Institute and the Office of Naval Research for support of their work under Project NR 031-339.

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# Work Hardening-Reannealing Cycle of Pure Silver

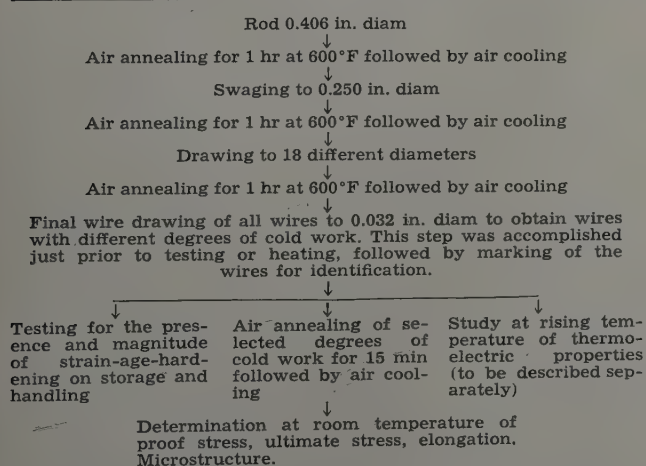
by Marian Balicki and Goldye Leeds

A SURVEY of literature reveals the scarcity of experimental evidence relating to work hardening and reannealing of silver.<sup>1-10</sup> With the exception of the well-known X-ray investigation of silver and other metals by W. A. Wood,<sup>11</sup> the effect of progressive cold working has not been studied. The determination of thermal stability of silver in the work-hardened state by means of isochronal or isothermal annealing has been confined apparently to very high reductions only. In the survey made, no study was encountered which endeavored to produce a complete picture of the changes in various properties due to cold working and subsequent reannealing. To fill these gaps and to assemble data that could be used for the determination of activation energies and of frequency coefficients of primary recrystallization, a systematic experimental approach, which was developed by one of the authors, has been applied to pure silver.

## Material and Processing

The silver used was Handy and Harman fine silver, with a spectroscopic analysis at the testing stage of Cu, 0.0001 to 0.001 pct; Te, 0.0001; Pb, Si, Ca, Mg, and Mn, traces. The material was supplied

Table I. Processing of Handy and Harman Silver for Testing



in the form of a rod 0.406 in. diam and was converted into test samples according to the procedure condensed in Table I. It should be mentioned that air annealing was adopted to simulate industrial practice, though it was realized that annealing in a neutral gas or in a vacuum would be preferred.

The usual precautions have been taken to eliminate any structural changes and property changes resulting from the storage of the samples prior to annealing or testing. Thus the wires were kept at the fully annealed stage, and the final wire drawing, which produced the desired degree of work hardening, was done just prior to the final annealing or testing. During the short waiting period, the samples were kept in a thermosflask filled with ice. Even with these precautions some strain-age-hardening or self-annealing could occur.

To test such a possibility, wires of different reductions were prepared in the manner adopted and portions of them were immediately tested. The remaining portions were similarly tested after different periods of storage, both at room and melting-ice temperature. Within experimental error, all samples obtained from a wire of a given percentage of reduction yielded identical values. This result qualified the material for further tests and interpretations, because it showed that either strain-age-hardening and self-annealing were absent, or that these effects fully balanced each other.

The final annealing was carried out in an electric resistance furnace automatically controlled to within  $\pm 10^\circ\text{F}$ . It was realized that the temperature fluctuations were greater than desired for this type of work. To diminish the errors due to fluctuations of temperature, the hot junction of the thermocouple was placed as close to the samples as possible; the time of soaking was reduced to 15 min; and the number of samples annealed at different temperatures was increased.

It will be seen from Table I that some tests were performed on the same material at rising temperature. These will be discussed elsewhere.

Room temperature testing was limited to the determination of some of the mechanical properties that are known to be additive in a degree sufficient to be used for indirect study of the kinetics of the reannealing process.<sup>4</sup> Tensile tests, carried out on a manually operated J. Camillon machine, accurate to within  $\frac{1}{4}$  lb, permitted the determination of the ultimate stress (U.S.) and of the 2 in. elongation, ( $A_2$ ). The proof stress ( $\sigma_p$ ) has been determined from a series of bend tests carried out on a Tinius Olsen Stiffness Tester by using the offset method. This involved accurate determination for each sample of load-angular deflection curves, finding a

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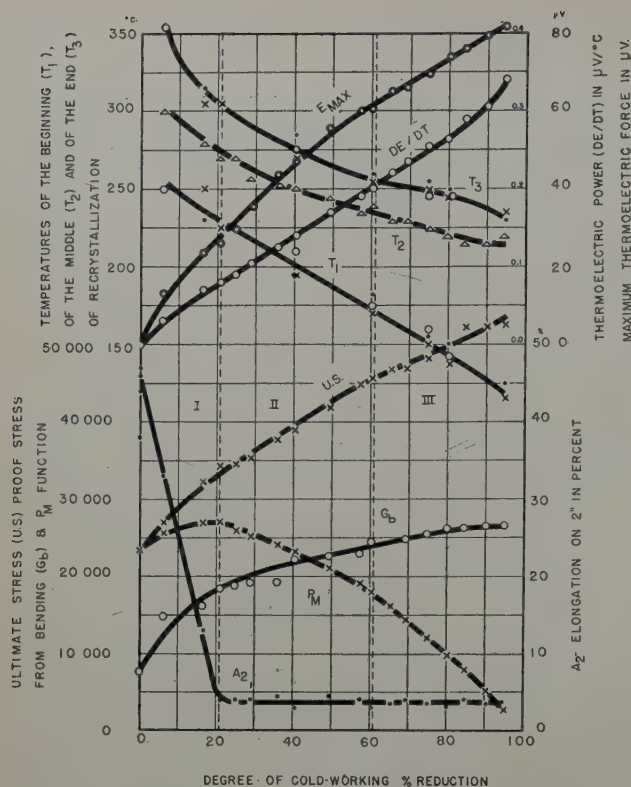


Fig. 1—Effect of cold work on properties of pure silver.

$A_2$  is the elongation on 2 in.,  $\sigma_b$ , the proof stress from bending test; U.S., the ultimate stress;  $p_m$ , Krupkowski's strength factor;  $dE/dt$ , the thermoelectric power of couples Ag cold-worked/Ag annealed;  $E_{max}$ , the maximum thermoelectric force developed by the same couples;  $T_1$ ,  $T_2$ ,  $T_3$ , the temperatures of the beginning, middle, and end of recrystallization respectively, all plotted vs. the percentage of reduction produced by room temperature drawing.

load responsible for  $5^\circ$  deflection, and calculating the corresponding stress from the bending formula. Values of proof stress thus obtained would be somewhat higher than those determined from tensile tests. This difference, which is of no real significance for the main purpose of the work, should be attributed to the adoption of a relatively large angle of permanent set, which brings the most stressed portion of the cantilever test piece well inside the plastic range. There, the bending formula, which is valid within the elastic range only, yields inflated values of stress.

### Results

The data obtained have been collected in Appendix 1.\* Figs. 1, 2, and 3 represent the findings graphically. Fig. 1 shows how a number of physical properties of fine silver change by cold working from 0 to 95 pct reduction. Elongation on 2-in. gage length  $A_2$ , for instance, rapidly decreases from its original value of 46 pct to a constant level of 3 pct, at about 21 pct reduction,  $z$ . Ultimate stress, U.S., and proof stress from bending,  $\sigma_b$ , exhibit an almost steady increase, with increasing reduction, though not quite the same in each case. Severe reduction of 95 pct more than doubles the starting values of these properties.

For fuller illustration of the effect of cold working on silver, Fig. 1 contains six additional curves. Two of these, namely, thermoelectric power,  $dE/dT$ , and maximum thermoelectric force,  $E_{max}$ , shown by thermocouples made of silver wires drawn to dif-

ferent reductions,  $z$ , and a standard fully annealed silver wire, show a steady increase as a function of the percentage of reduction. This increase, it will be seen, is very similar to the increase of ultimate and proof stress.

The strength change index,  $p_m$ , introduced by Krupkowski<sup>14</sup> has been calculated from ultimate stress data and values of the percentage of reduction

$z$ , by means of the relationship  $p_m = U.S. \left(1 - \frac{Z}{100}\right)$ .

It may readily be shown that  $p_m = \frac{P_{max}}{F_u}$ , where  $P_{max}$

is the breaking load and  $F_u$ , the section area prior to final wire drawing. It may be seen in the figure that this index slightly increases for low reductions to reach a shallow maximum at about 21 pct. This is followed by a steady decrease, slightly accelerated after 60 pct reduction.

The last three curves in the figure, namely,  $T_1$ ,  $T_2$ , and  $T_3$ , represent, as a function of the percentage of reduction, the characteristic temperatures of primary recrystallization, which is the phenomenon responsible for the main change in properties on reannealing. The data for plotting the  $T_1$  and  $T_3$  curves, illustrating the temperatures of the beginning and of the end of recrystallization, respectively, have been derived from Figs. 2 and 3; while data for the  $T_2$  curve, that is, the temperature of the middle of recrystallization, have been taken from studies of thermoelectric properties at rising temperature. It may be seen that in silver, as in other metals, the temperature range in which the main change in properties takes place on reannealing, is visibly lowered for higher reductions. Unlike other metals studied by this method, however, for reductions greater than 60 pct, silver exhibits an enlargement of the temperature range (vertical distance between  $T_3$  and  $T_1$  curves). It appears that the beginning of recrystallization is decreasing with reduction more rapidly than is the middle and the end of the process (Figs. 2 and 3).

An analysis of all the curves shown in Fig. 1 permits distinguishing three regions of plasticity. The first region between 0 and approximately 21 pct reduction is characterized by rapid increases or decreases in most of the curves. The limit of this region is quite well defined by the percentage of reduction at which elongation reaches its low value and by the maximum in the  $p_m$  curve. The second region between approximately 21 and 60 pct reduction shows a steady run in most of the curves. The border between the second and the third region is not easy to locate. This can best be done with reference to Fig. 4, which is a supplementation of Fig. 1. Wood<sup>15</sup> in his work on silver of similar purity to that used in this study, encountered a growing tendency toward self-annealing after 65 pct reduction, i.e., in the third region of plasticity.

Figs. 2 and 3 show the change in mechanical properties of wires with a selected percentage of reduction caused by 15 min reannealing at different temperature levels. All curves in these figures are well determined by suitably spaced experimental points. The proof stress  $\sigma_b$  curves show least deviation of experimental points, and they appear to be more suited for revealing small differences encountered than are the ultimate stress curves. For instance, proof stress and elongation curves for 80.1 and 60.5 pct reductions (Fig. 2) show quite well a small shift of the main change in the direction ex-

\* For Appendix 1 order Document 3360 from American Documentation Institute, 1719 N St., N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 in. high on standard 35 mm motion picture film) or \$1.00 for photocopies (6x8 in.) readable without optical aid.



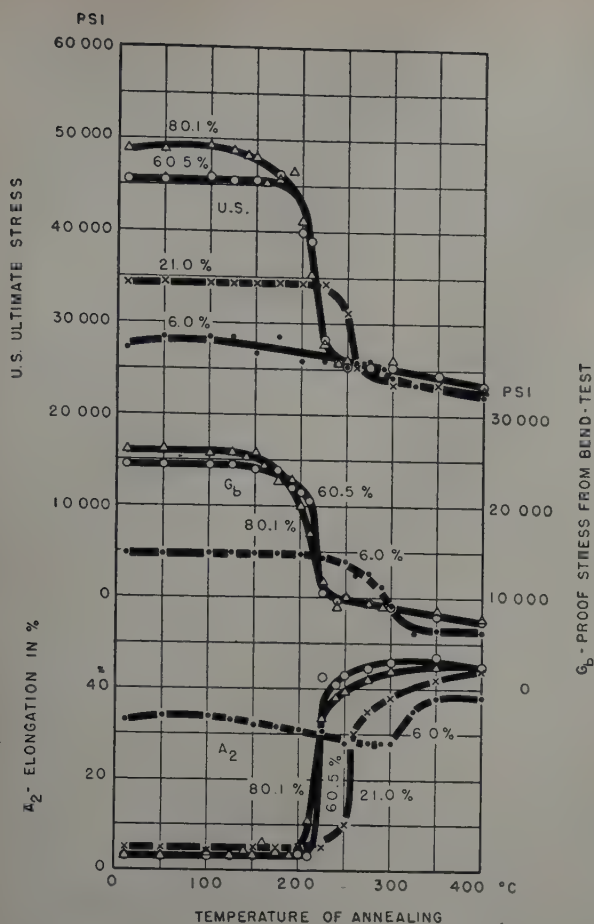


Fig. 2—Change in the mechanical properties of silver cold drawn to 6.0, 21.0, 60.5, and 80.1 pct reduction due to annealing for 15 min at the temperatures indicated.

pected, while the ultimate stress curves exhibit too great a scatter of points to permit any differentiation.

All the curves in Figs. 2 and 3 can be divided into three parts; two almost level and straight portions at low and high temperatures of annealing joined by a third curved portion. The temperature at which the low temperature straight portion joins the curved segment is that of the beginning of primary recrystallization, while the temperature at which the curved segment merges with the second straight portion is that of the end of recrystallization. Observation of the temperatures at which tangents drawn to the straight line portions depart from the curves yields the values of  $T_1$  and  $T_s$ . The temperatures of the beginning and of the end recrystallization obtained from all reannealing curves in Figs. 2 and 3 have been plotted on Fig. 1, using the same markers as in the curves from which they have been derived. There is some scatter of points, but it is not large. It may therefore be concluded that all three properties of the wire with a given percentage of reduction exhibit the main recrystallization change in the same range of temperature.

Microstructure of silver wires with different degrees of cold working has been studied at a magnification of 500X. In general, the structural changes revealed by this work follow the pattern exhibited by other metals on progressive work hardening and reannealing. Because of that only a very brief summary of results needs to be given. In the first region of plasticity, that is, for reductions lower than 21 pct, the microscope revealed the presence of slip lines, as well as a slight departure from equiaxiality of the original crystals. In the second and third re-

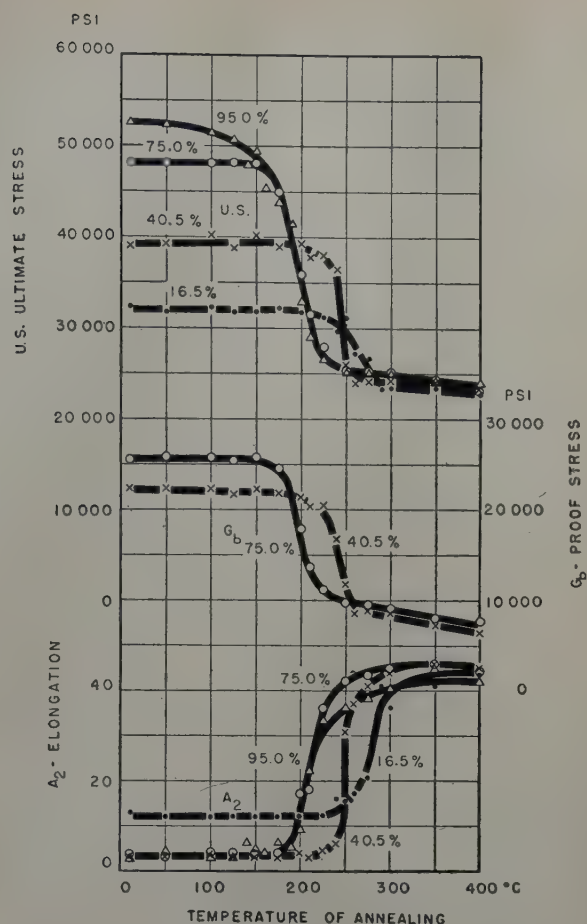


Fig. 3—Change in the mechanical properties of silver cold drawn to 16.5, 40.5, 75.0, and 95.0 pct reduction due to annealing for 15 min at the temperatures indicated.

gion of plasticity, a progressively better developed fibrous structure was observed. The effect of annealing was studied on wire with 40.5 pct reduction. Small annealed areas were first observed on samples annealed for 15 min at 225°C. The wire annealed at 250°C produced a structure almost completely free of work-hardened state. These results, when considered together with reannealing curves for  $z = 40.5$  pct in Fig. 3, permit a statement that the change in mechanical properties of cold-worked silver, as in other metals, is due to primary recrystallization; that is, the conversion of the work-hardened structure into a fully annealed, stress-and-distortion-free

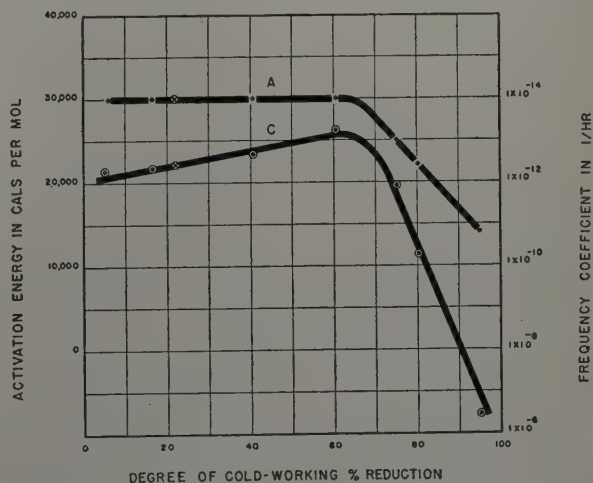


Fig. 4—Activation energies  $A$  and frequency coefficients  $C$  of primary recrystallization of cold-drawn silver as a function of the percentage of reduction.

one. As the main change in mechanical and physical properties on reannealing has been ascribed to "recovery" or "relaxation," it follows that these phenomena are identical with primary recrystallization.

### Activation Energy and Frequency Coefficient

The data secured from isochronal annealing experiments and collected both in Appendix 1 and Figs. 2 and 3 can be used for calculation of two coefficients, namely, the activation energy and the frequency coefficient of primary recrystallization. Since a number of suitably spaced reductions between 5 and 95 pct reduction have been tested, the change of these constants as a function of the degree of cold work ( $z$ ) can also be determined. The calculations are based on the fact that primary recrystallization is an activated process.<sup>12, 18</sup> In the absence of pronounced side phenomena such as strain-age-hardening and excessive crystal growth, primary recrystallization is described by the expression:

$$x = 1 - e^{-c, t, e^{-A/RT}}$$

or

$$\log \frac{1}{1-x} = c, t, e^{-A/RT}$$

In this expression,  $x$  is the fraction of a unit volume of a work-hardened metal sample which has fully recrystallized on subsequent reannealing. Depending on conditions of reannealing, i.e., on temperature of reannealing,  $T^\circ\text{K}$  and the time in hours,  $t$ ,  $x$  may acquire any value between 0 and 1. The expression also contains  $A$ , the activation energy of the recrystallization process,  $R$ , the gas constant, and  $k$ , the frequency coefficient.

For a given metal sample, having the same composition and history, the values  $A$  and  $C$  are constant. To find numerical values of these it is necessary to plot  $\log\log 1/(1-x)$  vs.  $1/T$ . The numerical

values of  $x$  required for this step can be secured from reannealing data such as those collected in Appendix 1, if the properties studied are additive to a degree sufficient for the purpose. The properties studied in the present work are considered as adequately fulfilling this condition. The calculation of the amount of the fully annealed state in partially annealed samples  $x$  has been obtained from the proportion:

$$x = \frac{(P_z - P_a)}{(P_z - P_0)}$$

when using properties which decrease on reannealing, viz., ultimate stress and proof stress from bending. When a property that increases on reannealing is used, such as elongation, both the numerator and the divisor in the proportion are multiplied by  $(-1)$ . In the above proportion,  $P_z$  designates the value of a property found when testing a fully cold-worked sample without any annealing;  $P_x$ , the value of the same property found after annealing for 15 min at temperature  $T^\circ\text{K}$ ; and  $P_0$ , the level of property values found in totally annealed samples.

With the exception of the data for  $z = 21.5$  pct all the data assembled in the Appendix have been used and values of  $\log\log 1/(1-x)$  calculated. These, whether derived from the values of ultimate stress, proof stress, or elongation of a given percentage of reduction of the wire, have been plotted on the same diagram vs. the inverse of the absolute temperature of annealing. The points for each percentage of reduction arranged themselves into straight lines. The spread of points present introduced some uncertainty as to the true position of the straight line. To secure straight lines, the slope of which would yield the value of activation energy  $A$ , five different observers were asked to determine their version of the slopes of the straight line for

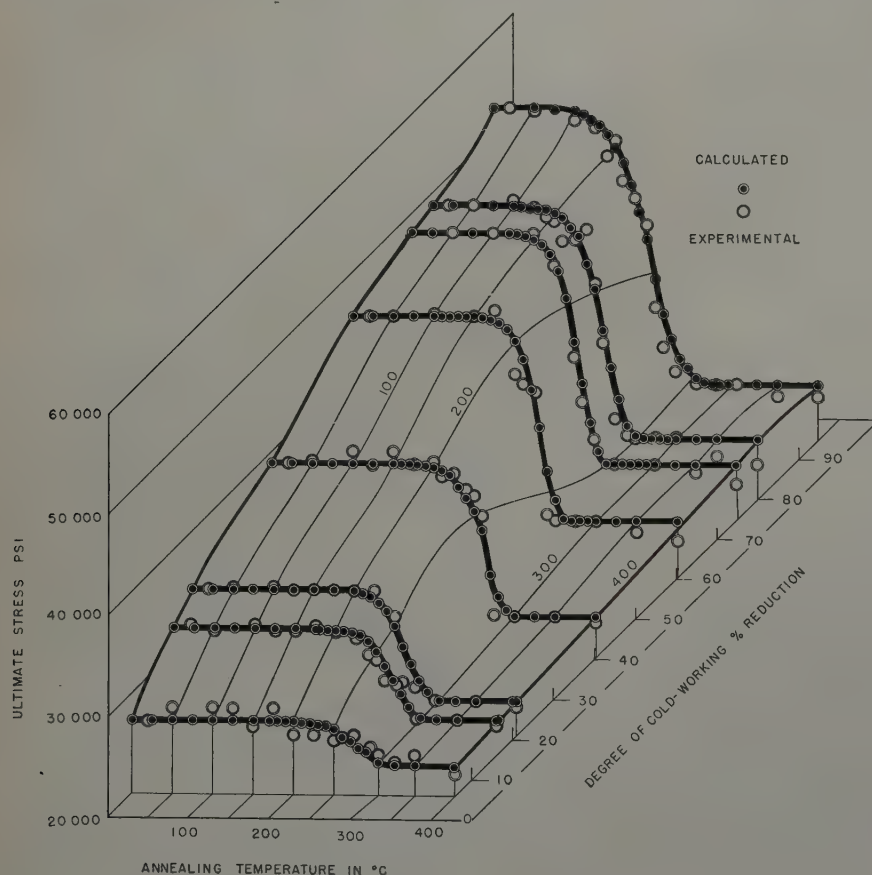
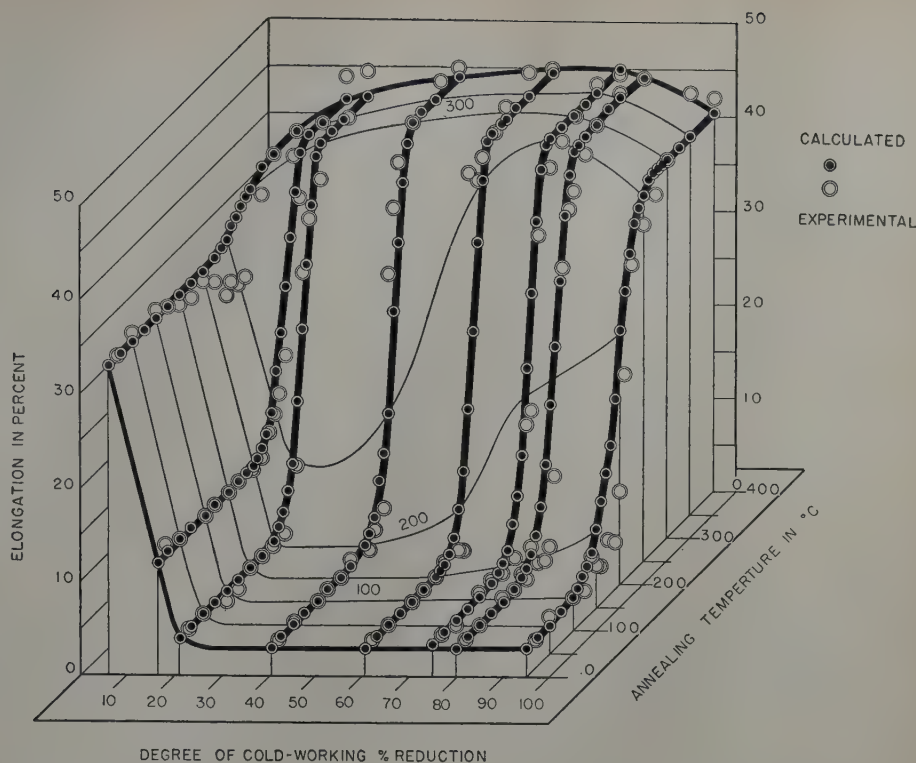


Fig. 5—Space diagram showing the agreement between the experimental and calculated values of the ultimate stress of silver cold drawn to the reductions indicated and subsequently annealed for 15 min at the temperatures indicated. Open circles, experimental; filled in circles, calculated.



Fig. 6—Space diagram showing the agreement between the experimental and calculated values of 2 in. elongation of silver cold drawn to the reductions indicated and subsequently annealed for 15 min at the temperatures indicated. Open circles, experimental; filled in circles, calculated.



each system of points. The slopes thus obtained resulted in average values of the activation energies and frequency coefficients of each degree of cold work. A plot of these coefficients vs. the corresponding percentage of reduction is given in Fig. 4. The values for 21 pct reduction have been obtained by interpolation. The differences between the different observers, alone, make these points uncertain to within  $\pm 4000$  cal per mol. It may be seen in Fig. 4 that the activation energy remains constant up to 65 pct of cold work and diminishes steadily for higher percentages of reduction. The constant level of activation energy is approximately at 30,000 cal per mol, a value found previously for copper, nickel, and iron.

The values of the frequency coefficient,  $c$ , are also plotted on Fig. 4. They arrange themselves into a curve which slowly increases up to about 60 pct reduction and subsequently decreases. This decrease is very rapid.

#### Verification of the Treatment Employed

There are two pertinent questions which demand an answer: 1—how accurately do the equations used in the treatment describe the course of reannealing, and 2—how well are the activation energy and the frequency coefficients determined? A positive answer to both questions can be secured by confronting the experimentally found values of three properties studied after 15 min annealing at different temperatures with corresponding values derived by calculation from the equations used. A reasonably good coincidence of calculated and experimental points should constitute a proof that both the equations employed, as well as the constants used, are sound. Too great a difference between the experimental and calculated values would indicate that either the equation or the constants are wrong. An additional investigation would then be necessary to secure an individual answer to the two questions.

The detailed calculations of the  $P_s$  values are omitted here. The steps involved in arriving at the

calculated  $P_s$  values are as follows: 1—substituting into the main equation numerical values of  $A$  and  $c$  found for silver with the percentage of reduction examined, together with numerical values of  $R$  and  $t = 15$  min; 2—finding numerical values of  $x$  from this equation for several assumed values of temperature,  $T$ ; 3—substituting these values of  $x$  into the auxiliary equation,  $x = (P_s - P_s)/(P_s - P_s)$ , together with numerical values of  $P_s$  and  $P_s$ ; and 4—solving this equation for  $P_s$ . The values of ultimate stress, proof stress, and 2 in. elongation thus obtained have been plotted against the assumed temperatures of annealing (filled double circles in Figs. 5, 6, and 7). The experimental data from Appendix 1 have also been plotted on the same diagram (open double circles). As may be seen from these figures, in which all results are collected, the calculated and experimental points lie as closely together as can be hoped for. Because the experimental and calculated curves coincide, a conclusion can be drawn that the equation used truly depicts the course of reannealing of silver, and that the numerical values of the activation energy as well as those of the frequency coefficients have been determined to a satisfactory degree.

#### Discussion

A few remarks concerning the curves of the activation energy and of the frequency coefficient, Fig. 4, are in order. Up to a 60 pct reduction, both these curves behave like similar curves for iron and nickel tested by this method. Here, the activation energy remains almost constant and at the same 30,000 cal level, while the frequency coefficient increases. Such a run of the curves is quite in conformity with the principles of the activation mechanism, though it is not entirely clear why all three metals should require the same activation energy for primary recrystallization.

Above the 60 pct reduction, that is, in the third region of plasticity, both the activation energy and the frequency coefficient of primary recrystalliza-

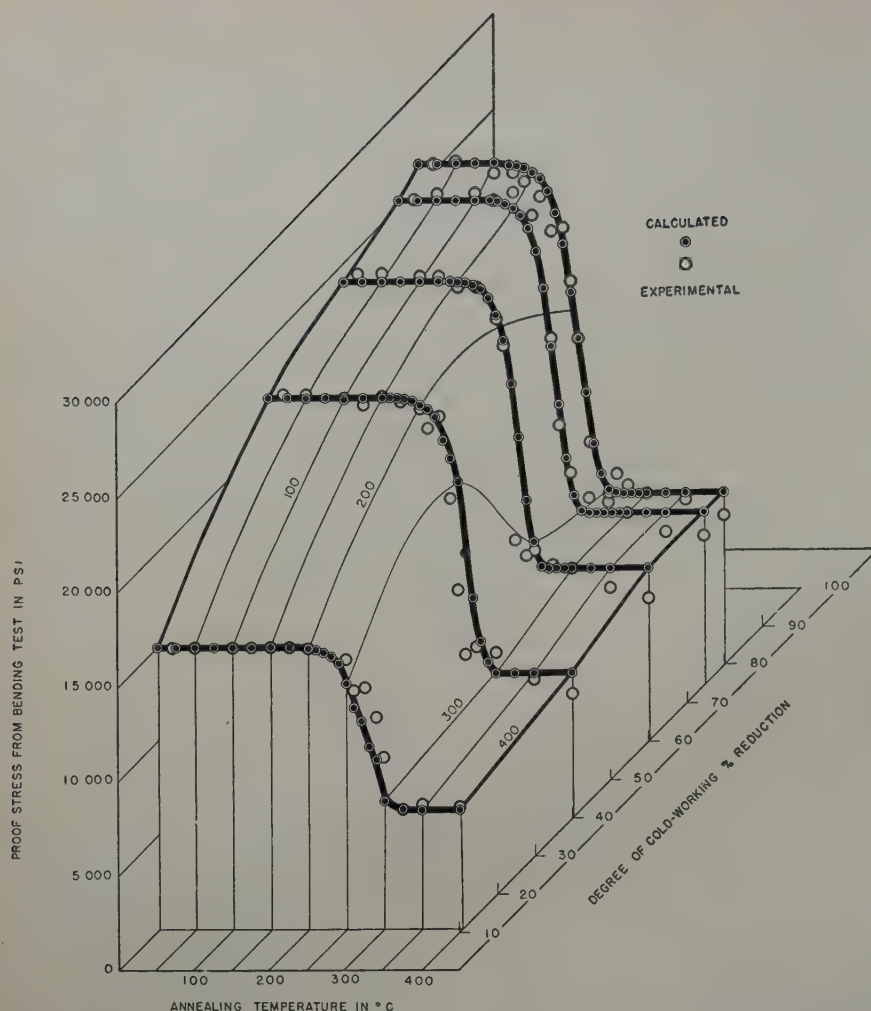


Fig. 7—Space diagram showing the agreement between the experimental and calculated values of the proof stress from the hardening of silver cold drawn to the reductions indicated and subsequently annealed for 15 min at the temperatures indicated. Open circles, experimental; filled in circles, calculated.

tion of silver diminish. This is unexpected, for, with the lowering of the activation energy, it would be reasonable to expect the frequency coefficient to increase. The verification treatment reveals (see Figs. 5, 6, and 7) approximately the same closeness of experimental and calculated points both below and above the 60 pct reduction. This means that the pairs of the frequency coefficients and activation energies, which determine the result of calculation, are quite accurate throughout the whole range of reduction studied. It appears from the above that the lowering of the activation energy and of the frequency coefficient after 60 pct reduction is real and that it is associated with the differences exhibited by reannealing curves after 60 pct reduction is passed. In the region above 60 pct reduction, the drop in properties extends over a longer interval of temperature; the end of recrystallization ( $T_s$ ) remaining about the same, while the beginning of recrystallization moves rapidly towards room temperature as the percentage of reduction increases, Fig. 1.

The behavior of this kind is no doubt a demonstration of the tendency to self-annealing, to which severely cold-worked silver is known to be prone. The work of Wood<sup>11</sup> reveals that silver, very similar in purity to that used in this work, started to self-anneal when 60 pct reduction was reached.

Thus, the unexpected lowering of the frequency coefficient when the activation energy decreases should be linked with the causes and the mechanism of self-annealing. As our knowledge of self-anneal-

ing is limited, the clarification of the issue raised by this work must be left for future research.

In view of the findings presented in this paper, it appears that the recovery of mechanical properties of cold-worked silver on reannealing is caused by primary recrystallization, that is, principally by conversion of the fully work-hardened state into a fully annealed one, and that this process is somewhat affected by the tendency for self-annealing, which occurs at reductions higher than 60 pct.

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# Effect of Rare-Earth Metals On the Properties of Extruded Magnesium

by T. E. Leontis

The specific effect of various rare-earth metals on the room- and elevated-temperature properties of magnesium has been evaluated. Alloys containing didymium exhibit the highest tensile and compressive strengths at room and elevated temperatures. All the rare-earth metals increase the creep resistance of extruded magnesium at temperatures in the range of 400° to 600°F, but the degree of enhancement depends on the temperature and on the concentration of the added metal.

THE effects of rare-earth metals on the properties of sand-cast magnesium were discussed in some detail in earlier paper by the author.<sup>1</sup> The present paper deals with the effect of the same alloying elements on the properties of extruded magnesium. This investigation also had as its aim the development of a wrought alloy having a better combination of room-temperature strength and ductility and elevated-temperature strength and creep resistance than is found in magnesium-Mischmetal-manganese alloys, which have been reported earlier.<sup>2-5</sup> The only known attempt to study wrought magnesium alloys containing pure cerium instead of Mischmetal was made by Mellor and Ridley.<sup>6</sup> They found that in the form of rolled bars there is a definite, optimum cerium content for creep resistance at 200°C and that the creep resistance of these alloys at 200°C is significantly improved by heat treatment at 550° to 580°C.

In the present investigation the compositional variation in mechanical properties of the following alloy systems<sup>7</sup> is presented: 1—magnesium-Mischmetal. 2—magnesium-cerium-free Mischmetal. 3—magnesium-didymium. 4—magnesium-cerium. 5—magnesium-lanthanum. Alloys containing predominantly praseodymium are not included in this series because of the lack of this material.

## Experimental Procedures

The alloying ingredients used in preparing the alloys described herein are the same as those reported in the earlier paper.<sup>1</sup> Cerium-free Mischmetal is the rare-earth mixture remaining when the cerium is removed from Mischmetal, which contains all the rare-earth metals as they occur naturally in monazite sand, the ore from which Mischmetal is produced. Removal of both cerium and lanthanum from Mischmetal leaves what is commonly called "didymium," consisting predominantly of neodymium and praseodymium. Although the composition of the particular batch of each metal used may differ somewhat from the analysis presented previously, these differences are not great enough to warrant repeat-

ing the specific composition of each material. The electrolytic magnesium used as the starting material in these alloys has the same typical analysis as that given in the earlier paper.<sup>1</sup>

The alloys were prepared in small laboratory melts applying all the necessary precautions for alloying rare-earth metals with magnesium described by Marande.<sup>7</sup> Most melts were large enough to cast one 3 in. diam billet 10 in. long. In a few cases, particularly the didymium-containing alloys, the lack of sufficient amounts of the rare-earth metal limited the size of the billet to 6 to 8 in. All billets were scalped to a diameter of 2 15/16 in. and faced to a length of 9 1/4 in. as limited by the size of the extrusion container.

The alloys were extruded into 1/2 in. diam rod on a 500-ton direct-extrusion press using a 3 in. container. The details of the extrusion step are: billet preheat, 925°F (2 hr); container temperature, 900°F; die temperature, 900°F; extrusion speed, 10 ft per min; reduction ratio, 36:1; and percent reduction, 97.3. The lower melting point of alloys containing didymium<sup>1</sup> necessitated reduction of the extrusion speed to 5 ft per min in order to prevent hot shorting during extrusion. Adequate lengths were cropped from both ends of each extruded rod to assure that all the material used for tests was extruded under uniform conditions.

Tensile and compressive properties at room temperature are reported in the several conditions of heat treatment. The ASTM designations are used to distinguish these conditions as follows:

T5—Direct age at 400°F (16 hr)

T4—Heat treat at 950°F (4 hr) for alloys containing didymium

T4—Heat treat at 1050°F (4 hr) for all other alloys

T6—T4 + age at 400°F (16 hr)

The lower heat-treating temperature for alloys containing didymium is necessitated by the lower melting point of these alloys. All heat treatments were conducted in electrically heated, circulating-air furnaces. A protective atmosphere containing 0.5 to 1.0 pct sulphur dioxide was used for the high temperature heat treatments.

Tension and creep specimens 6 1/2 in. long and compression specimens 1 1/2 in. long were cut from the extruded rod. A reduced section of 3/8 in. diam was machined on the tension specimens, whereas on the creep specimens a reduced section of 0.450 in. diam

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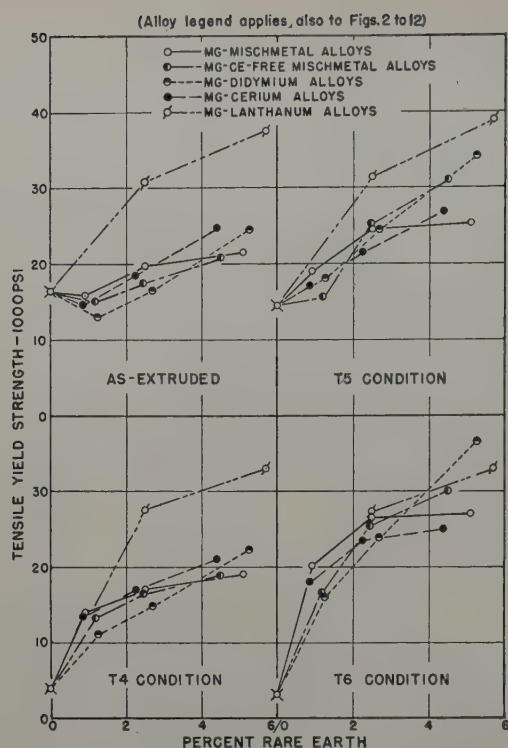


Fig. 1—Tensile yield strength at room temperature.

was used. The ends of the compression specimens were machined square with the cylindrical side, and the tests conducted on the full  $\frac{1}{2}$  in. diam without a reduced section. All tension and compression tests were conducted according to standard ASTM testing procedures. Elongation on the  $\frac{3}{8}$  in. reduced section was measured over a  $1\frac{1}{2}$  in. gage length. Yield strengths were determined by the offset method from autographic stress-strain curves at 0.2 pct deviation from the modulus line. Each result is the average of two tests.

Details of the equipment and methods of creep

testing have been described elsewhere.<sup>2,8</sup> Space does not permit the presentation of the complete creep data either in tabular or graphical form. Instead, the creep characteristics of each alloy are defined by the following three parameters:

- 1—Limiting stress to give 0.1 pct creep extension in 100 hr
- 2—Limiting stress to give 0.2 pct total extension in 100 hr
- 3—Limiting stress to give 0.5 pct total extension in 100 hr

These quantities were derived from log stress vs. log extension plots of the original data as described earlier.<sup>2,8</sup> The total extension figures include the creep extension as well as the initial extension resulting from application of the load. The brevity of these tests prohibits any great significance being ascribed to the measured creep rates, which consequently are not reported in this paper. The method of determining electrical conductivity has been described in an earlier publication.<sup>9</sup>

### Discussion of Results

**Effect of Extrusion Speed and Temperature:** In order to obtain the optimum properties, it is necessary to extrude the alloys under carefully selected conditions. The two most important variables in this process are temperature and speed. Reduction also has some effect on the properties of magnesium extrusions; however, in the case of extruded round rods, the properties are relatively insensitive to reduction over a wide range—as from 16:1 to 144:1. The reduction used in these experiments falls well within this range.

The effect of extrusion speed was determined on an alloy containing 5 to 6 pct Mischmetal + 1.8 pct Mn (according to the ASTM system of designation, this alloy is known as EM62). It was found that in the range of 5 to 25 ft per min, extrusion speed has no significant effect either on the room or elevated-temperature properties of rare-earth containing alloys. Grube, Davis, and Eastwood<sup>3</sup> were able to

Table I. Effect of Extrusion Temperatures and Heat Treatment

|                                    |    | Composition, Pct   |                    |                    |      |                    |                    |                    |      | Extrusion Conditions |                    |                    |      |
|------------------------------------|----|--------------------|--------------------|--------------------|------|--------------------|--------------------|--------------------|------|----------------------|--------------------|--------------------|------|
|                                    |    | Alloy              |                    |                    |      | Mischmetal         |                    |                    |      | Temperature, °F      |                    | Speed, Ft per Min  |      |
|                                    |    | A                  | B                  |                    |      | 5.7                |                    | 2.4                |      | 700                  |                    | 5                  |      |
|                                    |    |                    |                    |                    |      | 5.1                |                    | 1.8                |      | 900                  |                    | 10                 |      |
| Tensile and Compressive Properties |    |                    |                    |                    |      |                    |                    |                    |      |                      |                    |                    |      |
|                                    |    | Pct E*             | TYS                | CYS                | TS   | Pct E              | TYS                | CYS                | TS   | Pct E                | TYS                | CYS                | TS   |
| Room Temperature                   |    |                    |                    |                    |      |                    |                    |                    |      |                      |                    |                    |      |
| Alloy                              |    | As-Extruded        |                    |                    |      | T5 Condition       |                    |                    |      | T6 Condition         |                    |                    |      |
| A                                  |    | 10.0               | 29.2               | 28.4               | 38.7 | 8.0                | 31.2               | 30.0               | 39.5 | 11.6                 | 19.2               | 18.0               | 31.8 |
| B                                  |    | 8.3                | 24.7               | 20.4               | 36.0 | 6.7                | 29.3               | 20.1               | 38.4 | 5.7                  | 30.3               | 18.7               | 38.7 |
| Condition                          |    | 400°F              |                    |                    |      | 500°F              |                    |                    |      | 600°F                |                    |                    |      |
| A                                  | T5 | 35.0               | 16.6               |                    | 22.8 | 72.0               | 11.0               |                    | 16.3 | 222.0                | 3.9                |                    | 7.4  |
| A                                  | T6 | 23.6               | 14.4               |                    | 22.3 | 39.3               | 12.0               |                    | 19.4 | 105.5                | 6.6                |                    | 10.6 |
| B                                  | T6 | 11.5               | 18.2               | 17.7               | 25.0 | 24.0               | 14.4               | 14.4               | 22.3 | 72.5                 | 10.1               | 9.7                | 15.0 |
| Limiting Creep Stresses            |    |                    |                    |                    |      |                    |                    |                    |      |                      |                    |                    |      |
| 100-Hr Creep Limits — 1000 psi     |    |                    |                    |                    |      |                    |                    |                    |      |                      |                    |                    |      |
|                                    |    | 0.1 Pct Creep Ext. | 0.2 Pct Total Ext. | 0.5 Pct Total Ext. |      | 0.1 Pct Creep Ext. | 0.2 Pct Total Ext. | 0.5 Pct Total Ext. |      | 0.1 Pct Creep Ext.   | 0.2 Pct Total Ext. | 0.5 Pct Total Ext. |      |
|                                    |    | 400°F              |                    |                    |      | 500°F              |                    |                    |      | 600°F                |                    |                    |      |
| A                                  | T5 | 3.6                | 4.1                | 5.3                |      | 0.6                | 0.6                | 0.7                |      | 0.17                 | 0.20               | 0.30               |      |
| B                                  | T6 | 11.0               | 9.8                | 12.2               |      | 3.4                | 3.7                | 4.8                |      | 1.5                  | 1.7                | 2.0                |      |

\*Pct E — Percent elongation in 1.5 in.  
TYS — Tensile yield strength in 1000 psi  
CYS — Compressive yield strength in 1000 psi  
TS — Tensile strength in 1000 psi



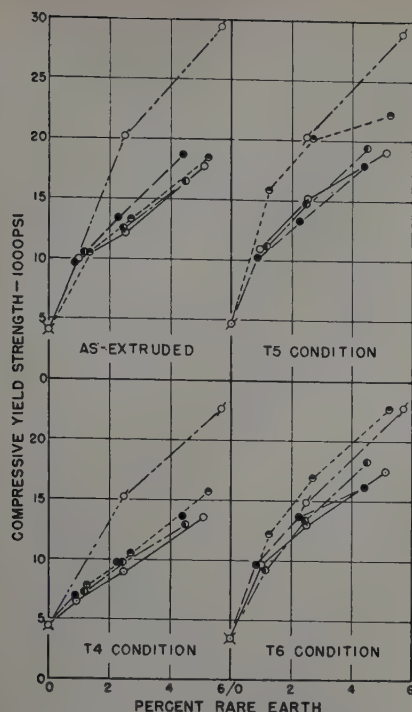


Fig. 2—Compressive yield strength at room temperature.

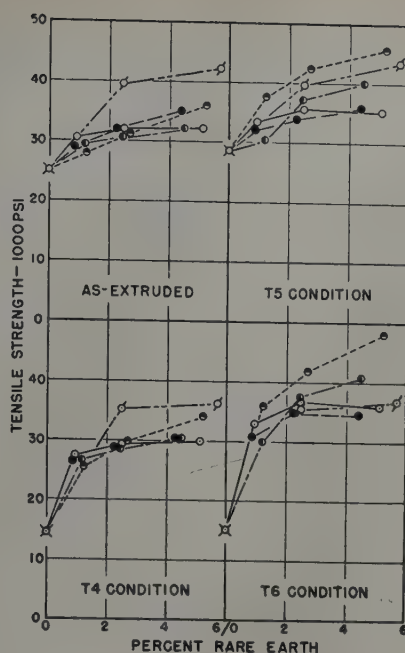


Fig. 3—Tensile strength at room temperature.

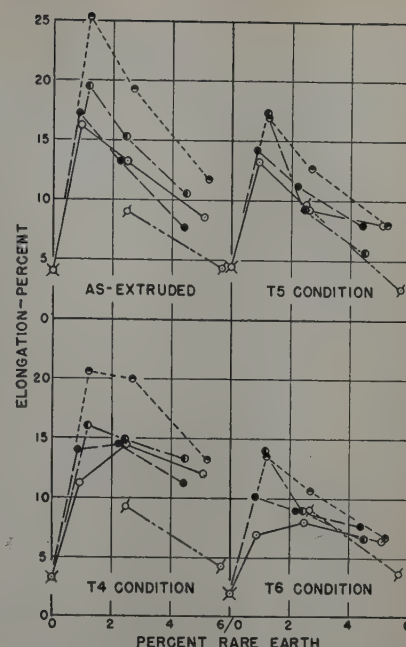


Fig. 4—Elongation at room temperature.

show some increase in strength with decreasing speed in the range of 27.3 to 4.11 in. per min.

Considerable work performed in our laboratory has shown that the maximum strength in magnesium-rare-earth alloys in the heat-treated and aged condition (T6) is developed by extruding at 900°F or higher. Results of one such experiment are presented in Table I. Although the lower extrusion temperature produces definitely higher yield strengths in the as-extruded and in the T5 conditions, significantly higher properties are obtained in the T6 condition by extruding at 900°F. Increasing the temperature above 900°F does not produce an increase in strength large enough to warrant use of such higher temperatures with the attendant greater wear on extrusion equipment and dies. The effect of extrusion temperature is more extensively presented by Grube, Davis, and Eastwood.<sup>3</sup>

**Effect of Heat Treatment:** The data included in Table I also show the pronounced beneficial effect that heat treating magnesium-rare-earth alloys has on the elevated-temperature strength and creep resistance. Whereas the alloy extruded at 700°F has the best combination of tensile and compressive properties at room temperature in the T5 condition, much higher strengths are exhibited by the same alloy in the T6 condition at elevated temperature. The superiority of the T6 condition is greater the higher the temperature of test. The comparison of creep properties is even more striking, as shown by the appropriate data in the same table.

Thus, it is apparent that in order to develop the maximum creep resistance and strength at elevated temperature in extruded magnesium-rare-earth alloys, the extrusion must be performed at 900°F or higher and the alloys must be heat treated and aged. Lower heat-treating temperatures produce proportionately lower properties. Increasing the heat-treating time beyond 4 hr does not produce any further advantage.

**Tensile Properties of Mg-Rare-Earth Alloys:** Complete tensile properties at room temperature,

300°, 400°, 500°, and 600°F have been determined on the five magnesium-rare-earth alloy systems as a function of composition. The results are presented graphically in the form of property vs. composition plots in Figs. 1 to 8 inclusive. Because of the small number of compositions investigated, the points have been joined by straight lines.

One of the most significant observations to be made from the room-temperature properties depicted in Figs. 1 to 4 is the marked difference in the degree of age hardening exhibited by the various alloy systems. In the as-extruded and in the heat-treated (T4) conditions, magnesium-lanthanum alloys show a decided superiority over all the other alloy systems, which differ little among themselves. However, magnesium-lanthanum alloys show no age hardening whatsoever, whereas all the other alloys increase in strength upon aging. In general, the degree of aging among the other four alloys increases in the following order: 1—magnesium-cerium. 2—magnesium-Mischmetal. 3—magnesium-cerium-free Mischmetal. 4—magnesium-didymium. This is a direct confirmation of the observations made on the corresponding cast alloys.<sup>1</sup> The result of these marked differences in age hardenability is to give magnesium-didymium alloys the highest strength in the heat-treated and aged condition (T6). In the directly aged state (T5 condition), the full extent of aging is not realized. Thus, magnesium-lanthanum alloys retain their as-extruded superiority in yield strength, but the tensile strength of the magnesium-didymium alloys is significantly higher than all the alloys.

It can be seen from Fig. 4 that the high strengths of the magnesium-lanthanum alloys are associated with relatively low ductility. Magnesium-didymium alloys have, in general, the highest elongation. The ductility of all magnesium-rare-earth alloys goes through a definite maximum at about 1 to 2 pct alloy content. The initial increase in elongation is a result of the marked reduction in grain size effected by the addition of small amounts of rare earths. The elongation decreases with further increases in rare-earth

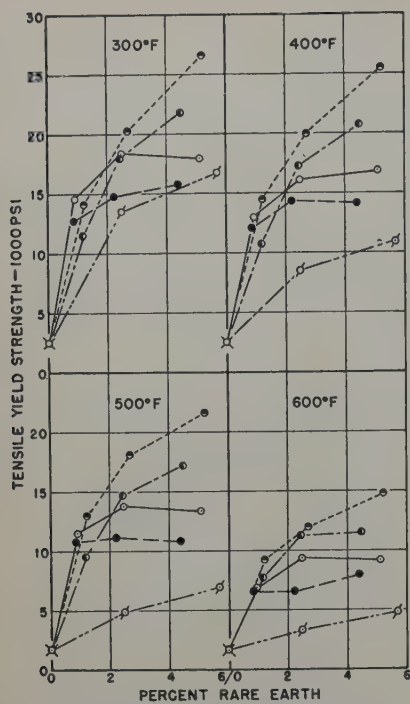


Fig. 5—Tensile yield strength at elevated temperatures T6 condition.

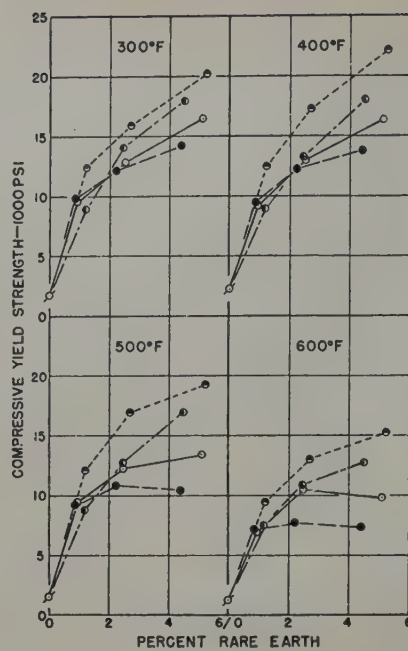


Fig. 6—Compressive yield strength at elevated temperatures T6 condition.

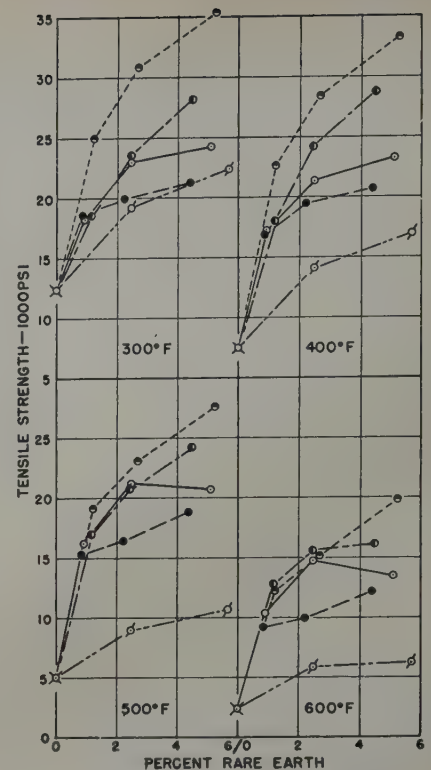


Fig. 7—Tensile strength at elevated temperatures T6 condition.

content because of the increasing amounts of undissolved intermetallic compounds.

The elevated-temperature tensile and compressive properties of magnesium-rare-earth alloys (Figs. 5 to 8) present a more straightforward picture. At all temperatures investigated in the range of 300° to 600°F, the alloys fall in the following order of decreasing strength: 1—magnesium-didymium. 2—magnesium-cerium-free Mischmetal. 3—magnesium-Mischmetal. 4—magnesium-cerium. 5—magnesium-lanthanum. The spread in the strength properties of the alloys increases with increasing alloy content. The low strength of magnesium-lanthanum alloys is associated with very high elongation. The other magnesium-rare-earth alloys do not show very great differences in ductility at elevated temperatures.

**Creep of Magnesium-Rare-Earth Alloys:** The creep resistance of the various magnesium-rare-earth alloys in the T6 condition at 400°, 500°, and 600°F is shown in Figs. 9, 10, and 11, respectively. The relative effects of the various rare-earth metals on the creep resistance of magnesium depend to a great extent upon the temperature of test and to some extent upon the composition. At 400°F, magnesium-lanthanum alloys are markedly inferior to

Fig. 8—Elongation at elevated temperatures T6 condition.

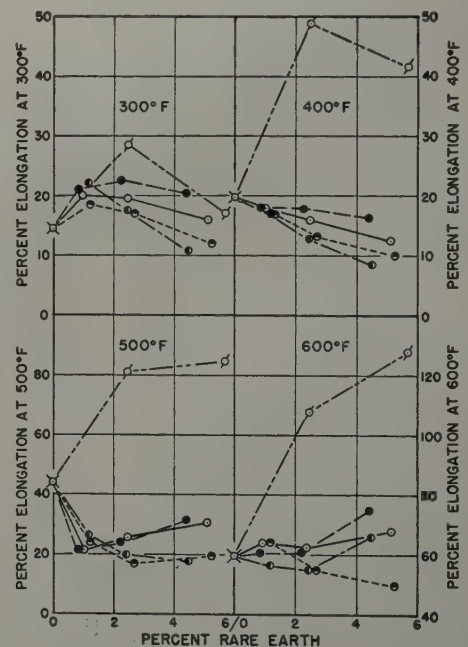


Table II. Tensile and Compressive Properties of Magnesium-Rare-Earth-Manganese Alloys

| Alloy                           | Pct E | TYS  | CYS  | TS           | Pct E | TYS  | CYS  | TS           | Pct E | TYS  | CYS  | TS           | Pct E | TYS  | CYS  | TS   |
|---------------------------------|-------|------|------|--------------|-------|------|------|--------------|-------|------|------|--------------|-------|------|------|------|
| Room Temperature                |       |      |      |              |       |      |      |              |       |      |      |              |       |      |      |      |
| As-Extruded                     |       |      |      | T5 Condition |       |      |      | T4 Condition |       |      |      | T6 Condition |       |      |      |      |
| 5.1 Mischmetal + 1.8 Mn         | 8.3   | 24.7 | 20.4 | 36.0         | 6.7   | 29.3 | 20.1 | 38.4         | 11.3  | 20.0 | 14.4 | 31.3         | 5.7   | 30.3 | 18.7 | 38.7 |
| 4.7 Ce-Free Mischmetal + 1.8 Mn | 8.7   | 22.9 | 19.6 | 35.0         | 6.0   | 32.4 | 21.4 | 41.7         | 11.3  | 21.6 | 14.7 | 31.8         | 4.7   | 35.3 | 19.7 | 42.4 |
| 4.8 Didymium + 1.5 Mn           | 11.0  | 25.2 | 19.3 | 37.2         | 7.0   | 35.7 | 22.3 | 45.0         | 13.0  | 22.9 | 16.6 | 34.4         | 6.7   | 37.7 | 23.0 | 47.3 |
| 4.9 Ce + 1.7 Mn                 | 7.7   | 26.8 | 20.9 | 36.8         | 7.3   | 29.2 | 19.8 | 37.2         | 11.0  | 21.7 | 14.7 | 30.7         | 6.7   | 27.9 | 17.3 | 36.2 |
| 1.85 Mn                         | 3.6   | 26.6 | 7.1  | 39.1         |       |      |      |              | 4.7   | 24.0 | 6.0  | 38.2         | 4.7   | 24.2 | 5.8  | 37.6 |
| T6 Condition                    |       |      |      |              |       |      |      |              |       |      |      |              |       |      |      |      |
| 300°F                           |       |      |      | 400°F        |       |      |      | 500°F        |       |      |      | 600°F        |       |      |      |      |
| 5.1 Mischmetal + 1.8 Mn         | 12.3  | 20.2 | 17.3 | 26.2         | 11.5  | 18.2 | 17.7 | 25.0         | 24.0  | 14.4 | 14.4 | 22.3         | 72.5  | 10.1 | 9.7  | 15.0 |
| 4.7 Ce-Free Mischmetal + 1.8 Mn | 10.4  | 23.5 | 17.4 | 30.0         | 8.0   | 22.6 | 19.5 | 29.0         | 14.0  | 18.9 | 17.3 | 25.7         | 53.0  | 14.0 | 13.6 | 18.9 |
| 4.8 Didymium + 1.5 Mn           | 10.4  | 27.7 | 22.7 | 35.0         | 9.0   | 25.6 | 22.2 | 31.3         | 17.0  | 22.2 | 20.9 | 27.7         | 54.2  | 15.3 | 14.9 | 19.8 |
| 4.9 Ce + 1.7 Mn                 | 16.6  | 16.7 | 15.6 | 23.4         | 13.5  | 15.0 | 14.6 | 23.5         | 28.2  | 11.4 | 11.3 | 19.7         | 64.5  | 8.1  | 8.8  | 12.8 |
| 1.85 Mn                         |       |      |      |              | 38.5  | 6.7  | 5.3  | 11.5         | 52.0  | 4.2  | 4.4  | 7.7          | 53.5  | 3.0  | 3.0  | 5.3  |



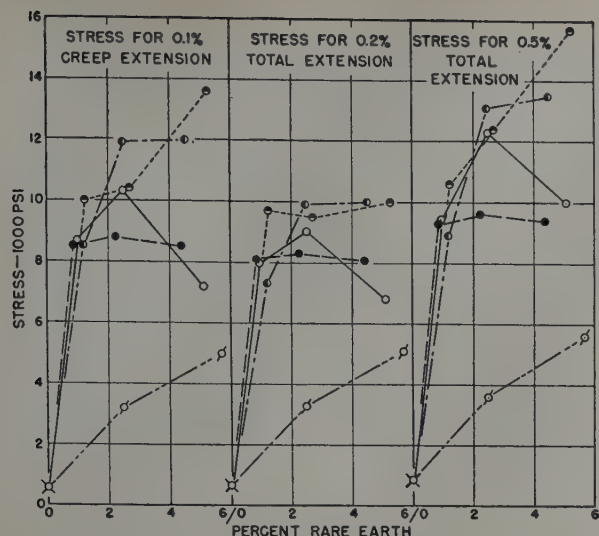


Fig. 9—100-hr limiting creep stresses at 400°F T6 condition.

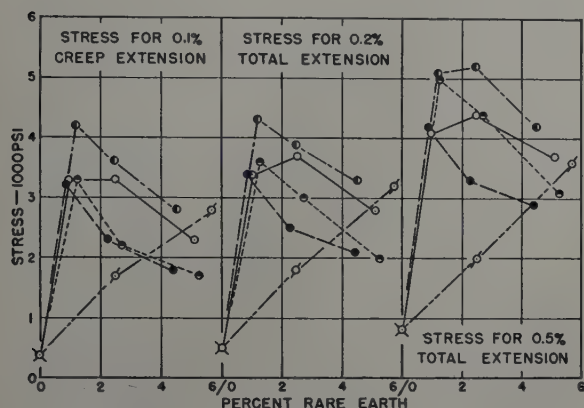


Fig. 10—100-hr limiting creep stresses at 500°F T6 condition.

all the other alloys and magnesium-didymium alloys have the highest creep limits, particularly at the higher end of the composition range investigated. The creep limits of magnesium-lanthanum alloys at 500° and 600°F vary with composition in a strikingly different manner from those of the other four alloy systems. Whereas the creep limits of the magnesium-lanthanum alloys increase regularly with the composition, those for alloys containing Mischmetal, didymium, cerium-free Mischmetal, and cerium rise to a maximum at about 1 to 2 pct rare-earth content and decrease sharply from this value with increasing alloy content. The result of these compositional trends is that the creep resistance of the magnesium + 5.7 pct La alloy is the highest observed at 600°F. Likewise at 500°F this composition tends to show higher creep resistance than is produced by the same quantities of the other solutes studied. The alloys

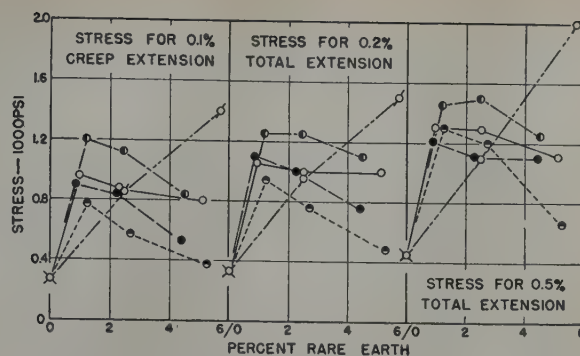


Fig. 11—100-hr limiting creep stresses at 600°F T6 condition.

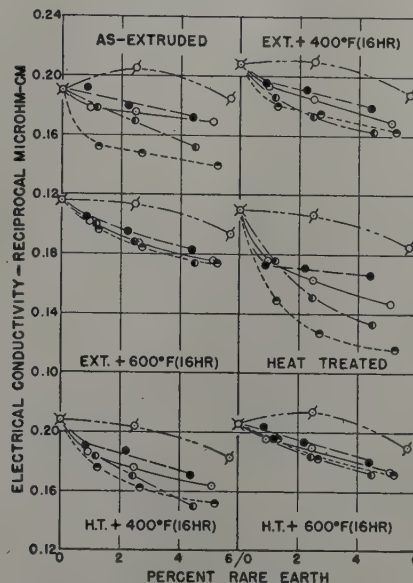


Fig. 12—Electrical conductivity at 95°F.

containing cerium-free Mischmetal exhibit the highest resistance to creep at the higher temperatures over the entire composition range. The decrease in creep resistance of all except the lanthanum-containing alloys may be attributed to a decrease in grain size from about 0.005 in. for the 1 pct alloy content to about 0.002 in. for the 5 pct alloy content. Magnesium-lanthanum alloys, on the other hand, retain a much finer grain size of about 0.0006 to 0.0009 over the composition range of 2.5 to 5.7 pct La as a result of the higher proportion of lanthanum in the form of compound. Perhaps the higher creep resistance of the lanthanum-containing alloys at 600°F results from the combination of fine grain size and a large amount of undissolved compound.

**Effect of Manganese on Magnesium + 5 Pct Rare-Earth Alloys:** In general, the addition of 2 pct Mn to magnesium + 5 pct rare-earth alloys increases

Table III. Limiting Creep Stresses of Magnesium-Rare-Earth-Manganese Alloys

|                                       |                                 | 100-Hr Creep Limits — 1000 psi |                         |                         |                         |                         |                         |                         |                         |                         |
|---------------------------------------|---------------------------------|--------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Condition                             | Alloy                           | 400°F                          |                         |                         | 500°F                   |                         |                         | 600°F                   |                         |                         |
|                                       |                                 | 0.1 Pct Creep Extension        | 0.2 Pct Total Extension | 0.5 Pct Total Extension | 0.1 Pct Creep Extension | 0.2 Pct Total Extension | 0.5 Pct Total Extension | 0.1 Pct Creep Extension | 0.2 Pct Total Extension | 0.5 Pct Total Extension |
| T6                                    | 5.1 Mischmetal + 1.8 Mn         | 11.0                           | 9.8                     | 12.2                    | 3.4                     | 3.7                     | 4.8                     | 1.5                     | 1.7                     | 2.0                     |
| T6                                    | 4.7 Ce-Free Mischmetal + 1.8 Mn | 12.8                           | 9.0                     | 15.5                    | 3.4                     | 3.8                     | 5.2                     | 0.94                    | 1.2                     | 1.6                     |
| T6                                    | 4.8 Didymium + 1.5 Mn           | 12.0                           | 9.9                     | 15.5                    | 2.3                     | 2.7                     | 4.5                     | 0.52                    | 0.64                    | 0.90                    |
| T6                                    | 4.9 Ce + 1.7 Mn                 | 8.6                            | 8.1                     | 10.2                    | 3.3                     | 3.5                     | 4.3                     | 1.8                     | 2.1                     | 2.5                     |
| As-extruded                           | 1.85 Mn                         | 1.9                            | 2.2                     | 2.8                     |                         |                         |                         | 0.60                    | 0.78                    | 1.0                     |
| T6                                    | 1.85 Mn                         | 2.3                            | 2.6                     | 3.4                     |                         |                         |                         |                         | 0.94                    | 1.2                     |
| Heat treated, water quenched and aged | 1.85 Mn                         | 2.3                            | 2.7                     | 3.6                     |                         |                         |                         | 1.2                     | 1.3                     | 1.7                     |



Fig. 13—Mg + 5.08 pct Mischmetal as-extruded. X100.



Fig. 14—Mg + 5.23 pct didymium as-extruded. X100.

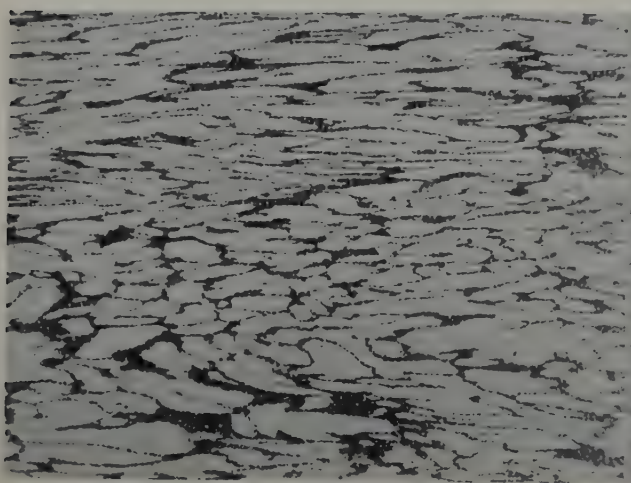


Fig. 15—Mg + 5.69 pct lanthanum as-extruded. X100.

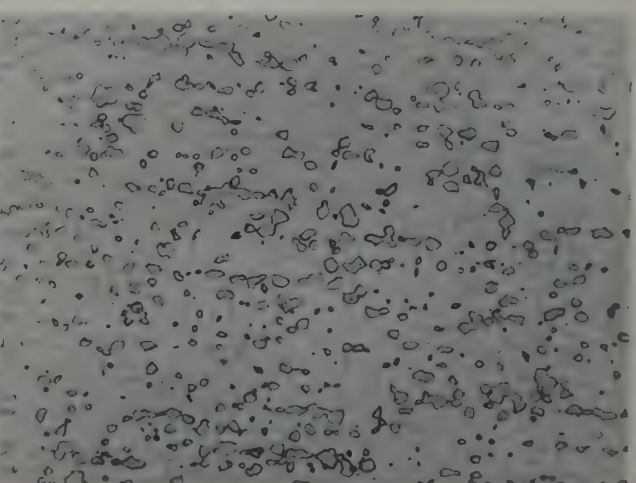


Fig. 16—Mg + 5.08 pct Mischmetal T6 condition. X250.



Fig. 17—Mg + 5.23 pct didymium T6 condition. X250.

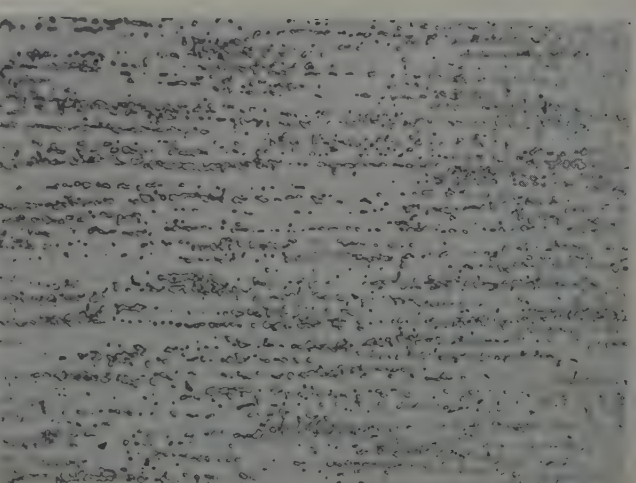


Fig. 18—Mg + 5.69 pct lanthanum T6 condition. X250.

the strength properties by 1000 to 2000 psi at all temperatures (Table II). The room temperature tensile properties of the binary magnesium + 1.85 pct Mn alloy, extruded under the same conditions as the magnesium-rare-earth alloys, are comparable to those of the latter alloys. However, the compressive yield strength of the binary magnesium-manganese alloy is much lower. Magnesium + 1.85 Mn alloy, however, does not exhibit the same degree of temperature resistance that the rare-earth alloys show.

Manganese also effects a definite improvement in the creep resistance of magnesium-rare-earth alloys (Table III). Much the same order of relative creep resistance is maintained among the various magnesium-rare-earth alloys even with the addition of manganese. This is not true at 600°F, where the alloy containing pure cerium has the highest creep limits and the Mischmetal-containing alloy is second. The creep characteristics of magnesium + 1.85 Mn have been determined in various conditions of



Table IV. Comparison of Optimum Didymium and Mischmetal Alloys

| Composition         | Tensile and Compressive Properties |      |      |      |          |      |      |      | Creep Limits<br>(1000 psi)<br>400°F |                               |                               |
|---------------------|------------------------------------|------|------|------|----------|------|------|------|-------------------------------------|-------------------------------|-------------------------------|
|                     | Room Temperature                   |      |      |      | 400°F    |      |      |      | 0.1 Pct<br>Creep<br>Extension       | 0.2 Pct<br>Total<br>Extension | 0.5 Pct<br>Total<br>Extension |
|                     | 1000 psi                           |      |      |      | 1000 psi |      |      |      |                                     |                               |                               |
|                     | Pct E                              | TYS  | CYS  | TS   | Pct E    | TYS  | CYS  | TS   |                                     |                               |                               |
| 2.69 Pct Didymium   | 10.6                               | 23.8 | 16.9 | 41.7 | 13.2     | 20.0 | 17.2 | 28.4 | 10.4                                | 9.5                           | 12.4                          |
| 2.47 Pct Mischmetal | 8.0                                | 26.4 | 13.3 | 37.1 | 16.0     | 16.1 | 13.0 | 21.4 | 10.3                                | 9.0                           | 12.3                          |
| 5.08 Pct Mischmetal | 6.7                                | 27.0 | 17.6 | 36.0 | 12.5     | 16.9 | 16.3 | 23.2 | 7.2                                 | 6.8                           | 10.0                          |

heat treatment. Whereas at 400°F this alloy cannot compare with the rare-earth alloys, at 600°F in the heat-treated, quenched, and aged condition, its creep limits are not much lower than those of the magnesium-manganese-Mischmetal alloy. Quenching the magnesium-1.85 Mn alloy from the heat-treating temperature effects a significant improvement in the creep resistance at 600°F. This treatment, however, was not found to have any effect on the tensile properties. Grube, Davis, and Eastwood<sup>8</sup> found the same behavior in this composition. Furthermore, these investigators showed that in alloys containing Mischmetal and manganese, no significant improvement in creep resistance is realized by quenching instead of air cooling from the heat-treating temperature.

**Electrical Conductivity:** The results of conductivity measurements (Fig. 12) show trends similar to those found in the sand-cast alloys. The low solubility of lanthanum in magnesium is again demonstrated by these data. No special significance should be attached to the maxima in the curves for magnesium-lanthanum alloys. Two possible explanations that might be proposed for this phenomena are: 1—differences in impurity content, and 2—differences in degree of preferred orientation.

**Metallography:** Selected micrographs of some of the magnesium-rare-earth alloys are shown in Figs. 13 to 18 inclusive. All the structures were revealed by etching with the standard glycol etchant which contains 75 parts ethylene glycol, 24 parts distilled water, and 1 part concentrated nitric acid. The as-extruded structures are given at a magnification of 100 diam. In alloys containing Mischmetal (Fig. 13) and didymium (Fig. 14), as well as cerium-free Mischmetal and cerium, the compound is present in the form of stringers of discrete particles. The magnesium-lanthanum alloy (Fig. 15), however, reveals many characteristics of the cast structure. The compound is present as clusters of small particles resembling a cast eutectic and in many parts of the structure the compound completely outlines the cast grains. These structural differences in the alloys correlate well with the as-cast microstructure. It was shown in the earlier paper<sup>1</sup> that in alloys containing mixtures of rare-earth metals, the eutectics are highly divorced and thus upon extrusion result in stringers of individual particles. Magnesium-lanthanum and magnesium-cerium alloys, on the other hand, form extremely fine eutectics in the cast state with the divorcement tendency being the least in the magnesium-lanthanum alloys. The extruded magnesium-cerium alloys show a slight indication of the eutectic, as in the magnesium-lanthanum alloys, but the slower freezing rate of a 3-in. diam billet as compared to a cast test bar probably leads to considerable divorcement of the eutectic in the magnesium-cerium alloys.

In Figs. 16, 17, and 18 the microstructures of the magnesium-Mischmetal, magnesium-didymium, and

magnesium-lanthanum alloys in the T6 condition show that the heat treatment results in considerable solution of compound in the two former alloys and in marked coalescence of the undissolved compound in all three alloys. It is clear from these micrographs and from observations on the other alloys that the order of increasing solid solubility in magnesium of these metals is: 1—lanthanum, 2—cerium, 3—Mischmetal, 4—cerium-free Mischmetal, and 5—didymium. These observations agree well with the conductivity measurements, Fig. 12. All the alloys containing about 1 pct rare earths also have significant amounts of undissolved compound except the magnesium + 1.23 pct didymium alloy. The latter has only a trace, indicating that its solid solubility limit in magnesium must be close to this composition.

### Summary

1—Data have been presented to show the specific effects of various rare-earth metals on the room and elevated-temperature properties of extruded magnesium.

2—Alloys may be rated in the following order of decreasing tensile and compressive properties at room and elevated temperatures and creep resistance at 400°F: 1—magnesium-didymium, 2—magnesium-cerium-free Mischmetal, 3—magnesium-Mischmetal, 4—magnesium-cerium, 5—magnesium-lanthanum.

3—Magnesium-didymium alloys do not maintain their superiority in creep resistance over the other alloys at 500° and 600°F. The highest creep resistance over the entire composition range at these temperatures is exhibited by magnesium-cerium-free Mischmetal alloys. High-lanthanum alloys are exceptional in creep resistance at 600°F.

4—It is possible to develop equivalent creep resistance at 400°F with a more favorable combination of strength and ductility at room temperature and higher strength at elevated temperature by using 2 to 3 pct didymium rather than 2 to 5 pct Mischmetal. These effects are illustrated in Table IV.

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# Preferred Orientation in Zirconium

by R. K. McGeary and B. Lustman

The textures produced in zirconium by cold and hot rolling, and by recrystallization above and below the transformation temperature were determined. Thermal expansivities were measured in the thickness, transverse, and rolling directions of preferentially oriented zirconium and were correlated with the texture scatter in these directions.

PREVIOUS investigations have indicated that minor differences between hexagonal close-packed metals of similar axial ratio may appear with respect to the textures produced both on cold rolling and on subsequent recrystallization. In the case of magnesium, beryllium, and titanium, metals of axial ratio similar to that of zirconium, the ideal orientations produced by rolling are fundamentally the same, although marked variance is reported in the degree and type of scatter about the mean orientation; in those instances where recrystallization textures were observed, they were reported to be similar to the rolling textures. Measurement of the anisotropy of thermal expansion of both rolled and recrystallized zirconium could not be correlated satisfactorily with the textures reported for the above metals, and therefore a study was made of the preferred orientations produced in zirconium. Reported below are the textures produced in zirconium by cold and hot rolling, and recrystallization above and below the transformation temperature, together with the results of thermal expansion measurements.

## Determination of Preferred Orientation

Two types of zirconium were investigated: 1—"crystal bar" zirconium obtained from the Foote Mineral Co., produced by the thermal decomposition of zirconium tetraiodide, and 2—zirconium ingot obtained from the Bureau of Mines prepared by melting sponge zirconium in a graphite resistor vacuum furnace in a graphite crucible.

The major impurities present in the two materials used are listed in Table I. Several of the pole figures were later checked with 0.03 pct hafnium crystal bar material and the results were identical with those to be shown for the 1.5 pct hafnium material.

The materials were cold rolled to 0.014 in. in thickness as shown in Table II.

Specimens were cut from the 0.014 in. thick rolled sheets and etched to thicknesses of 0.002 to 0.010 in. Such specimens were used for exposures up to a 50° to 60° angle between the beam and plane of the specimen; for higher angles a wire shape, similar to that described by Bakarian,<sup>1</sup> was formed on an end of the original 0.014 in. sheet. A fine-bladed abrasive

cut-off wheel was used to slot the sheet and to form the cylindrical cross-section. The wire shaped ends were then etched to 0.006 to 0.010 in. in diam. Although absorption of X-rays in the wire-shaped specimens does not vary with angle of rotation, the line width around the diffraction rings was not uniform, because the wire was narrower than the X-ray beam, and this condition caused some uncertainty in the estimation of azimuthal intensities. Furthermore, scanning was not practicable with this type of specimen so that spottiness of the rings due to large grain size was excessive for specimens which had been heated above about 650°C. Nevertheless, satisfactory information could be obtained for high angle exposures from the negatives by the use of both types of specimens.

Transmission Laue photograms were taken using unfiltered molybdenum radiation (47.5 kv, 18 ma) and a 0.025 in. pinhole. With the film 8 cm from a 0.005 in. thick specimen exposures of about 30 min were adequate. For specimens with a coarse grain size, a device that scanned about 0.15 sq in. of sheet surface was used.

An attempt was made to plot the pole figures by use of an X-ray spectrometer as described by Norton.<sup>2</sup> However, for the particular technique used, the intensity variations obtained were not considered definite enough to give reliable results, especially for the large grained recrystallized and transformed specimens. This method was therefore abandoned in favor of the standard photographic method.

Nine exposures were taken of each specimen: seven exposures with the beam perpendicular to the rolling direction and at 0°, 10°, 20°, 35°, 50°, 65°, and 80° to the transverse direction, and two exposures with the beam perpendicular to the transverse direction and at 60° and 80° to the rolling direction. Additional exposures were then made where necessary. The intensity variations of the diffraction rings were estimated by eye. It was usually possible to estimate 3 degrees of intensity from the photograms but in some cases 2, 4, or 5 degrees were estimated.

## Experimental Results

The preferred orientation was determined for the following treatments: 1—cold-rolled, 2—low temperature rolled, 3—cold-rolled surface layer, 4—cross-rolled, 5—hot-rolled, 6—recrystallized below the transformation temperature, and 7—recrystallized above the transformation temperature.

1—Cold-Rolled Textures: The slip plane in hexag-

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onal close-packed metals is the basal {0001} plane. During cold rolling this plane would be expected to rotate into the plane of the sheet by slip along the  $\langle 11\bar{2}0 \rangle$  directions. With such a slip mechanism the principal ideal orientation produced by cold rolling would be expected to consist of basal planes parallel to the rolling plane and either  $\langle 11\bar{2}0 \rangle$  or  $\langle 10\bar{1}0 \rangle$  directions parallel to the rolling direction.

For magnesium with an axial ratio ( $c/a = 1.624$ ) similar to that of zirconium (1.589), Caglioti and Sachs<sup>8</sup> found the {0001},  $\langle 11\bar{2}0 \rangle$  orientation, with the scatter greater in the rolling direction than in the transverse direction. Bakarian,<sup>1</sup> using purer magnesium than Caglioti and Sachs, found the same basal plane orientation but no directional orientation of the digonal axes. He showed also that the rolling texture is affected by the presence of certain impurities; 0.2 pct Ca caused a splitting of the central maximum area of the pole figure.

The basal plane pole figure of cobalt by Wasserman<sup>4</sup> indicates a splitting of the maximum area but no directionality of scatter.

Smigelskas and Barrett<sup>5</sup> observed a {0001},  $\langle 10\bar{1}0 \rangle$  orientation in the case of beryllium; this is the first observation that the  $\langle 10\bar{1}0 \rangle$  direction may lie in the rolling direction for close-packed hexagonal metals. Considerably more scatter in the transverse than in the rolling direction is apparent.

The pole figures of Clark<sup>6</sup> for cold-rolled titanium indicate that the hexagonal axis is inclined in the transverse direction about  $30^\circ$  from the rolling plane with the  $\langle 10\bar{1}0 \rangle$  direction in the rolling direction.

Burgers and Jacobs<sup>7</sup> pole figures of cold-rolled zirconium show, as do those of beryllium, the major scatter to be in the transverse direction. However, their pole figure of the {10 $\bar{1}$ 0} planes indicates a tendency for the  $\langle 11\bar{2}0 \rangle$  direction to lie in the rolling direction.

The pole figures of cold-rolled Bureau of Mines zirconium obtained in the present investigation for the three principal planes, {0002}, {10 $\bar{1}$ 0}, and {10 $\bar{1}$ 1}, are shown in Fig. 1a, b, and c. The pole figures of crystal bar zirconium are fundamentally the same as those of Bureau of Mines zirconium but with less scatter in the transverse direction. The average orientation best describing the maximum intensity areas, shown by the double circle points in Fig. 1, is that shown in the schematic drawing of Fig. 7a, which represents the basal planes parallel to the rolling direction but inclined from the rolling plane about  $30^\circ$  in the transverse direction, and with a  $\langle 10\bar{1}0 \rangle$  direction in the rolling direction. This orientation is most readily appreciated by consideration of the prism-plane {10 $\bar{1}$ 0}, and pyramidal-plane {10 $\bar{1}$ 1} pole figures. The diffraction photograms of Fig. 8a and b also indicate the  $30^\circ$  transverse tilt of the c-axis: four maxima intensity arcs appear at the 7, 8, 10, and 11 o'clock positions of the outer {10 $\bar{1}$ 1} ring of Fig. 8a, while maxima intensity arcs appear only at the 7 and 11 o'clock positions in Fig. 8b where the specimen was rotated  $20^\circ$  about the rolling direction.

2—*Low Temperature Rolling*: It was thought that the slip mechanism of zirconium might change with temperature as is observed in the case of magnesium, and that the change might be reflected in the rolling texture. Therefore, a piece of crystal bar

Table I. Composition of Materials Used

| Impurity       | In Crystal Bar, Pct | In Melted Bureau of Mines Sponge, Pct |
|----------------|---------------------|---------------------------------------|
| Hf             | 1.5                 | 1.5                                   |
| C              | 0.02                | 0.09                                  |
| O <sub>2</sub> | 0.02                | 0.08                                  |
| Fe             | 0.01-0.05           | 0.14                                  |

zirconium was rolled 95 pct at liquid nitrogen temperature. The texture of this material is in all respects similar to that of the crystal bar rolled at room temperature.

3—*Surface-Layer Texture*: It is often the case in wire drawing or cold rolling that the textures observed on the surface are different from those in the body of the metal because of inhomogeneity of the deformation process. The surface texture of Bureau of Mines zirconium was determined on a specimen coated on one side with wax and etched from 0.014 to 0.002 in. in thickness. The pole figures for this specimen did not reveal a new orientation but only a slight sharpening of the cold-rolling texture.

4—*Cross-Rolled Texture*: A square specimen of Bureau of Mines zirconium, which had previously been hot rolled, was cold rolled 90 pct by rotating the square  $90^\circ$  after each pass through the rolls. Each reduction was about 3 pct of the total reduction. The pole figures of Fig. 2 indicate that scatter in the transverse direction has been eliminated and that the cross rolling has resulted in a texture consisting of a basal plane parallel to the rolling plane, a  $\langle 10\bar{1}0 \rangle$  direction parallel to one rolling direction, and a  $\langle 11\bar{2}0 \rangle$  direction parallel to the other rolling direction. It would hardly be expected that such an orientation would be stable on cross rolling, but it would rather be expected that a double orientation with some  $\langle 10\bar{1}0 \rangle$  directions parallel to each rolling direction would be observed. However, if the rolling process is idealized as a combination of tension in the rolling direction and compression in the normal direction, and if a  $\langle 10\bar{1}0 \rangle$  direction were stabilized in the one rolling direction by duplex slip along  $\langle 11\bar{2}0 \rangle$  directions, then, in the direction transverse to this, the  $\langle 11\bar{2}0 \rangle$  direction would similarly be stabilized by duplex slip. To test the effect of orientation prior to cross rolling, a slab of as-cast ingot zirconium, which would not be expected to show any prior orientation, was cross rolled, and also exhibited a  $\langle 10\bar{1}0 \rangle$  direction parallel to the one rolling direction and a  $\langle 11\bar{2}0 \rangle$  direction parallel to the other.

5—*Hot-Rolled Texture*: With the exception of beryllium,<sup>5</sup> there is no information on the orientations produced by hot rolling hexagonal close-packed metals. For this metal the type of orientation for rolling temperatures as high as  $800^\circ\text{C}$  does not change.

Table II. Rolling Schedule

| Material        | Type Rolling | Rolling Temperature | Reduction in Thickness, Pct |
|-----------------|--------------|---------------------|-----------------------------|
| Crystal bar     | Straight     | Room temperature    | 95                          |
| Bureau of Mines | Straight     | Room temperature    | 96                          |
| Bureau of Mines | Straight     | $850^\circ\text{C}$ | 92                          |
| Bureau of Mines | Cross        | Room temperature    | 90                          |

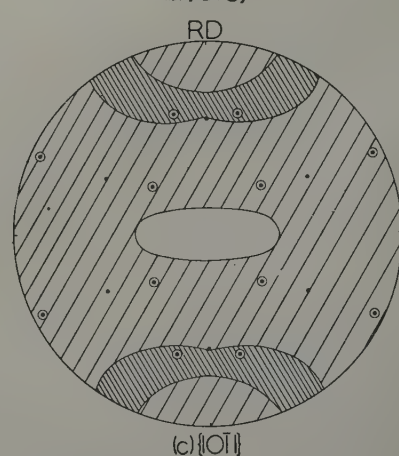
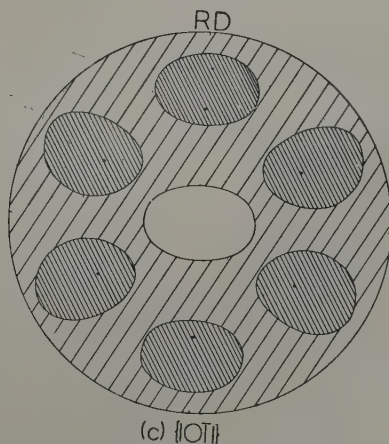
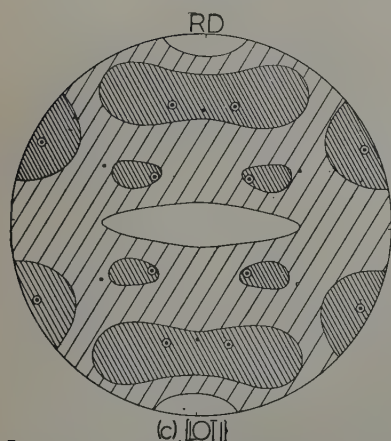
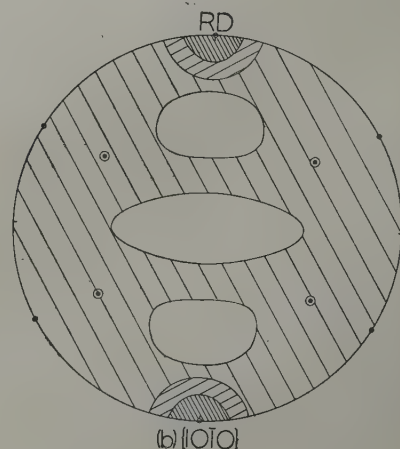
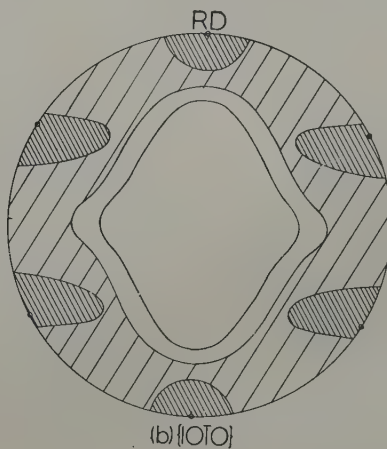
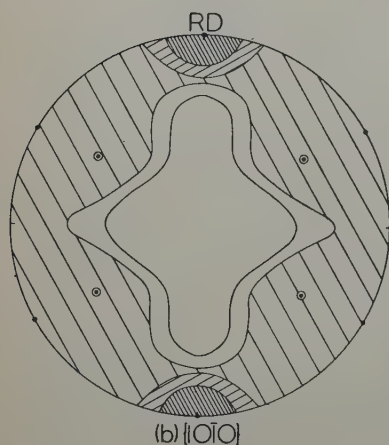
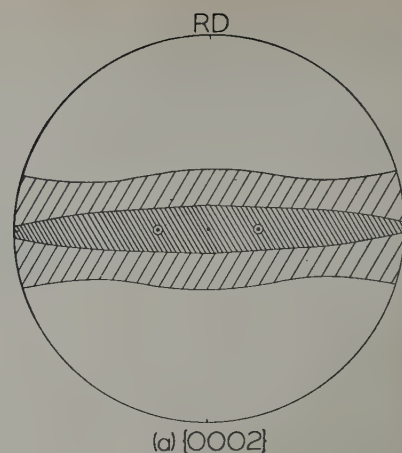
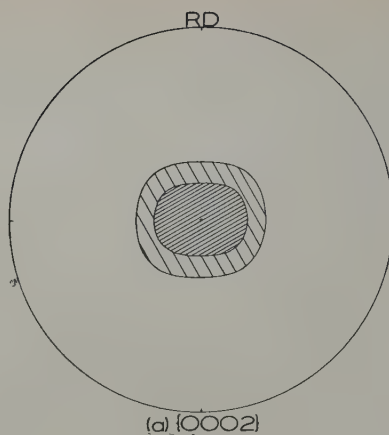
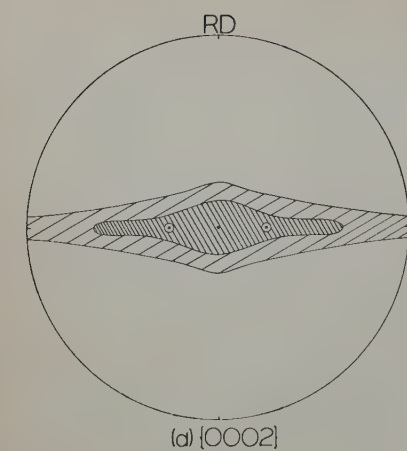


Fig. 1—Pole figures for cold-rolled Bureau of Mines zirconium.

● indicates {0002} || rolling plane and [10-10] || rolling direction.  
○ indicates {0002} rotated 30° about rolling direction.

Fig. 2—Pole figures for cross-rolled Bureau of Mines zirconium.

● indicates {0002} || rolling plane and [10-10] || rolling direction.

Fig. 3—Pole figures for hot-rolled (850°C) Bureau of Mines zirconium.

● indicates {0002} || rolling plane and [10-10] || rolling direction.  
○ indicates {0002} rotated 30° about rolling direction.

Hot rolling was performed on a specimen of Bureau of Mines zirconium plate, which was placed in a close-fitting steel jacket with  $\frac{3}{8}$  in. thick walls, all the seams of which were then welded gas tight. The jacket helped in maintaining the proper temperature of the sample and also in protecting it from oxidation. The total deformation at a temperature of 825° to 850°C was about 92 pct reduction in thickness. The pole figures for this sample, Fig. 3, indicate that the texture is essentially the same as the cold-rolled texture but has much more scatter in the transverse direction.

6—*Recrystallization Textures:* The textures that result when cubic metals are rolled and recrystallized are greatly varied and at present cannot be correlated successfully with any general theory. For

these metals the recrystallization textures may be the same as, or may be different from, the deformation texture, or no preferred orientation may result on recrystallization. For hexagonal close-packed metals there has been very little work done on rolling-recrystallization textures or the factors influencing the textures. Zinc and magnesium were found to retain their rolling textures at recrystallization temperatures up to the highest temperatures investigated, 400° and 600°F respectively.<sup>5</sup> The 700°C recrystallization textures of beryllium were also found to be the same as the deformation textures.<sup>5</sup> The basal plane pole figure of Clark<sup>6</sup> for titanium indicates that the recrystallization texture is the same (differing in degree) as the cold-rolled texture. However, a comparison of his photograms for the



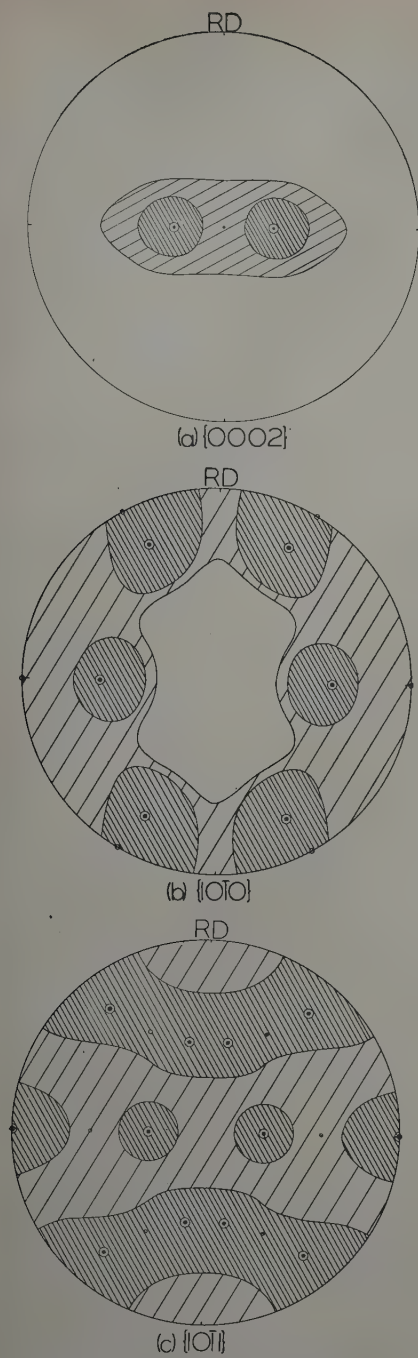


Fig. 4—Pole figures for cold rolled and recrystallized (650°C) Bureau of Mines zirconium.

• indicates {0002} || rolling plane and [11 $\bar{2}$ 0] || rolling direction.  
○ indicates {0002} rotated 30° about rolling direction.

{10 $\bar{1}$ 0} and {10 $\bar{1}$ 1} rings with the pole figures and photograms obtained in the present case for zirconium indicates that a rotation of the digonal axes about the hexagonal axis has taken place for titanium. Zirconium will be shown to undergo a 30° rotation of this type when recrystallized.

a—*Cold-Rolled Recrystallization Textures*: Specimens of the 0.014 in. thick cold-rolled sheet zirconium were recrystallized at 650°C. The specimens were sealed in evacuated glass tubes and were put into a hot furnace for 5 min (recrystallization was found to be complete in this time). The recrystallization pole figures for Bureau of Mines zirconium are shown in Fig. 4. The pole figures for recrystallized crystal bar are almost identical to those shown for the Bureau of Mines zirconium. A well-defined tex-

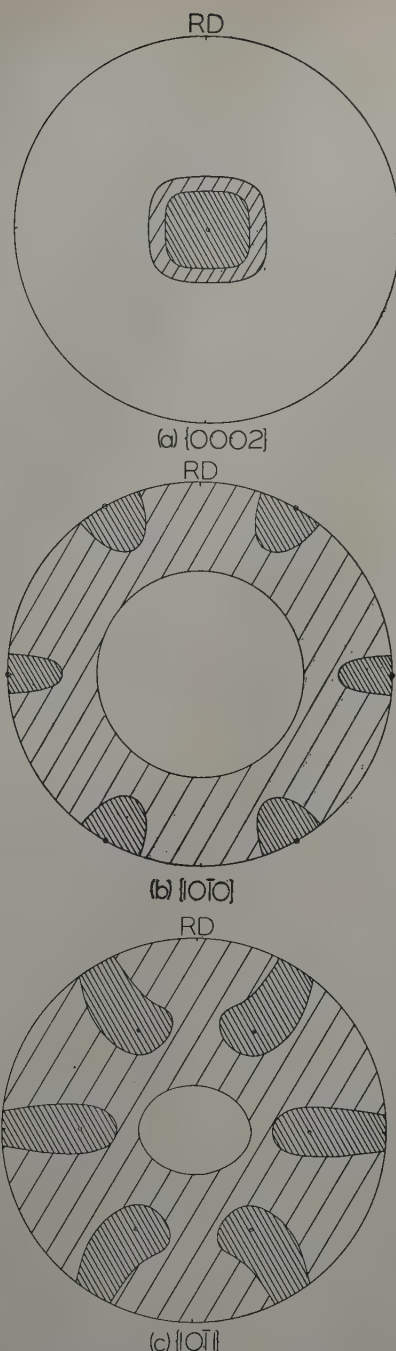


Fig. 5—Pole figures for cross-rolled and recrystallized (650°C) Bureau of Mines zirconium.

• indicates {0002} || rolling plane and [11 $\bar{2}$ 0] || rolling direction.

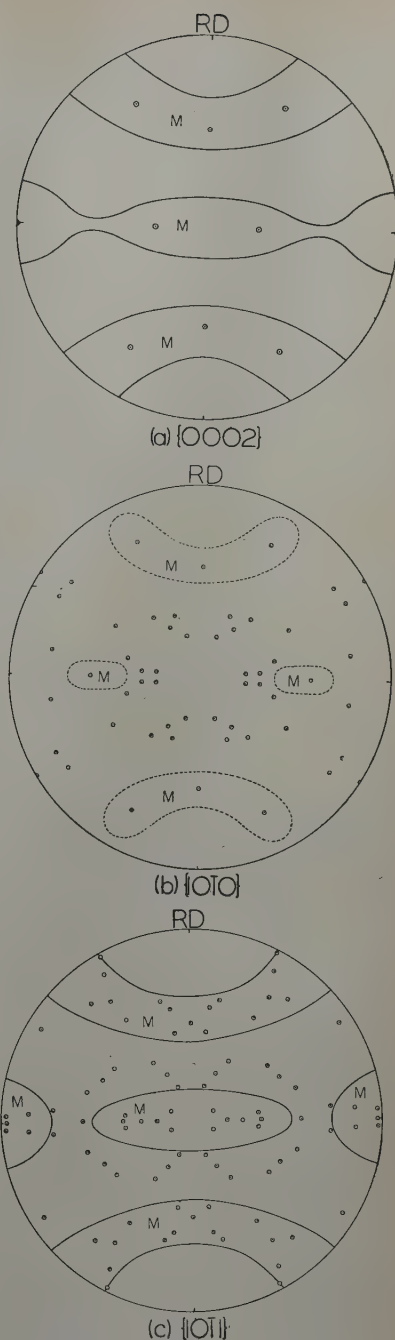


Fig. 6—Pole figures for Bureau of Mines zirconium heated above transformation temperature.

Points indicate calculated pole positions for Burgers' transformation mechanism from an ideal recrystallization orientation. Maximum intensity areas marked M.

ture fundamentally different from the rolling texture was observed. A schematic drawing of the average orientation best explaining the maxima areas of the pole figures is shown in Fig. 7b. The basal planes are inclined to the plane of the sheet at an angle of about 30° in the transverse direction and the <11 $\bar{2}$ 0> direction is parallel to the rolling direction.

Pole figures were plotted for a recrystallized sample which was later found to have been overheated. The heating temperature was below the transformation temperature (862°C), since there was no metallographic evidence of a transformation structure, and was estimated to lie between 800° and 862°C. The pole figures of this specimen were very similar to those of the specimen recrystallized at 650°C, so

the recrystallization texture apparently does not vary in this temperature range.

The average orientation described above may also be considered as a twinned orientation with a  $\{10\bar{1}1\}$  first-order pyramidal twinning plane perpendicular to the rolled sheet and parallel to the rolling direction. The usual twinning planes for close-packed hexagonal metals are the  $\{10\bar{1}2\}$  second-order pyramidal planes. No metallographic evidence of twinning could be found in recrystallized zirconium.

Burgers and Jacobs<sup>7</sup> found the  $\langle 11\bar{2}0 \rangle$  direction parallel to the rolling direction and the basal plane parallel to the rolling plane, while in a later work Burgers, Fast, and Jacobs reported the following ideal fiber textures for zirconium wire:

Cold drawn wire— $\langle 10\bar{1}0 \rangle$  direction parallel to wire axis

Recrystallized wire— $\langle 11\bar{2}0 \rangle$  direction parallel to wire axis

If a reasonable correspondence is assumed between the wire axis and the rolling direction of sheet material, the observations for wire coincide with the present observations for rolled zirconium. It is readily apparent that the rotation of axes described above does occur if a comparison of the innermost  $\{10\bar{1}0\}$  rings of Fig. 8a and c is made. The former figure, a photogram made with the X-ray beam perpendicular to the plane of the cold-rolled sheet, shows maxima in the 6 and 12 o'clock positions, indicating a  $\langle 10\bar{1}0 \rangle$  direction parallel to the rolling direction, while the latter figure, a similar photogram of the recrystallized sheet, shows maxima at the 5, 7, 11, and 1 o'clock positions, indicating a  $\langle 11\bar{2}0 \rangle$  direction parallel to the rolling direction.

For rolled zirconium, the  $\langle 10\bar{1}0 \rangle$  direction was always found to be parallel to the rolling direction. With flow parallel to the rolling direction by duplex slip on basal planes in  $\langle 11\bar{2}0 \rangle$  directions, it would be expected that either a  $\langle 10\bar{1}0 \rangle$  or  $\langle 11\bar{2}0 \rangle$  direction would lie parallel to the rolling direction. Having once established either direction parallel to the rolling direction it would seem impossible to change

it by further working. To find if the preferred  $\langle 11\bar{2}0 \rangle$  direction parallel to the rolling direction observed in the case of recrystallized zirconium could be shifted by further working, the following experiments were performed. The original cold-rolled crystal bar zirconium was recrystallized to place a  $\langle 11\bar{2}0 \rangle$  direction parallel to the rolling direction as shown in the photogram of Fig. 9c. The specimen was then cold rolled an additional 86 pct and the photogram of Fig. 9d taken. It may be noted that once more the  $\langle 10\bar{1}0 \rangle$  direction is parallel to the rolling direction. Subsequent recrystallization again caused a rotation of the  $\langle 11\bar{2}0 \rangle$  into the rolling direction. These direction changes correspond to a  $30^\circ$  rotation about the hexagonal axis. It is interesting to point out the similarity of the above results to those of Beck, Sperry, and Hu<sup>8</sup> who found the maximum rate of growth in the case of recrystallization of aluminum to be at orientations corresponding to a  $30^\circ$  to  $45^\circ$  rotation about a  $\langle 111 \rangle$  axis with respect to the original orientation.

b—*Cross-Rolled Recrystallization Texture*: It was shown in Section 3 and Fig. 7c that the cross-rolled deformation texture had the following ideal orientations: the basal plane parallel to the rolling plane, a  $\langle 10\bar{1}0 \rangle$  direction parallel to one rolling direction, and a  $\langle 11\bar{2}0 \rangle$  direction parallel to the other rolling direction. The pole figures of Fig. 5 showing the recrystallization texture of this specimen indicate a new orientation, shown in the schematic drawing of Fig. 7d: the basal plane is parallel to the rolling plane (as in the deformation orientation) but a  $\langle 11\bar{2}0 \rangle$  direction is oriented parallel to the rolling direction which in the rolled condition was parallel to a  $\langle 10\bar{1}0 \rangle$  direction, and a  $\langle 10\bar{1}0 \rangle$  direction is oriented parallel to the other rolling direction which showed a  $\langle 11\bar{2}0 \rangle$  direction in the rolled condition. This change corresponds to a  $30^\circ$  rotation about the hexagonal axis.

7—*Texture after Heating above the Transformation Temperature*: The allotropic transformation temperature of zirconium has been established as  $862^\circ \pm 5^\circ\text{C}$  by dilatometric and thermal analysis.<sup>10</sup> Above this temperature zirconium is body-centered cubic and below it, hexagonal close-packed. Burg-

Table III. Previous Data on Thermal Expansivity of Zirconium

| Material        | Condition      | Treatment                                                                                                         | Temperature Range, °C | Coefficient of Thermal Expansion $\times 10^{-6}$ per °C  | Reference |
|-----------------|----------------|-------------------------------------------------------------------------------------------------------------------|-----------------------|-----------------------------------------------------------|-----------|
|                 | CR foil        |                                                                                                                   | 0-100                 | 2.5 (parallel to c-axis)                                  | 13        |
| Bureau of Mines | Rolled sheet   |                                                                                                                   | 25-300                | 14.3 (parallel to a-axis) (by X-ray diffraction)          | 14        |
| Crystal bar     | Drawn wire     |                                                                                                                   | Room temp.            | $10.3 \pm 0.5$ (parallel to c-axis)                       | 15        |
|                 | Wire           |                                                                                                                   |                       | $4.5 \pm 0.5$ (parallel to a-axis) (by X-ray diffraction) | 16        |
|                 |                |                                                                                                                   | 20-200                | 6.3                                                       |           |
|                 |                |                                                                                                                   | 200-300               | 5.4                                                       |           |
|                 |                |                                                                                                                   | 300-400               | 6.4                                                       |           |
|                 |                |                                                                                                                   | 400-500               | 6.9                                                       |           |
|                 |                |                                                                                                                   | 500-600               | 7.9                                                       |           |
|                 |                |                                                                                                                   | 600-700               | 8.4                                                       |           |
| Crystal bar     |                |                                                                                                                   | 20-600                | 8.9                                                       | 17        |
| Bureau of Mines | Cold rolled    | Rolled 400°-600°C from ingot; cold rolled additional 50 pct                                                       | 25-500                | 4.69                                                      | 18        |
| Bureau of Mines | Hot rolled     | Rolled 400°-600°C from ingot                                                                                      | 25-500                | 4.10                                                      |           |
| Bureau of Mines | Recrystallized | Rolled 400°-600°C from ingot; heated 600°C                                                                        | 25-500                | 4.98                                                      | 18        |
| Bureau of Mines | Transformed    | Rolled 400°-600°C from ingot; heated to 1400°C                                                                    | 25-500                | 5.39                                                      | 18        |
| Bureau of Mines | Transformed    | Rolled 400°-600°C from ingot; heated to 1400°C; reheated to 950°C                                                 | 25-500                | 6.60                                                      | 18        |
| Bureau of Mines | Recrystallized | Rolled 400°-600°C from ingot; heated to 1400°C; reheated to 950°C; cold worked additional 50 pct; heated to 600°C | 25-500                | 6.50                                                      | 18        |
| Crystal bar     | Recrystallized | Swaged 90 pct R.A.; heated to 600°C                                                                               | 25-500                | 5.20                                                      | 18        |
| Crystal bar     | Transformed    | Swaged 90 pct R.A.; heated to 1400°C                                                                              | 25-500                |                                                           |           |
| Powder compact  | Transformed    | Sintered at 1000°-1100°C                                                                                          | 25-500                | 6.17                                                      | 18        |
|                 |                |                                                                                                                   |                       | 6.40                                                      | 18        |



ers,<sup>11</sup> by X-ray analysis of selected portions of crystal bar zirconium which were single crystals of the cubic modification at the deposition temperature, found the following orientation relationships between the hexagonal close-packed and the body-centered cubic modifications:

BCC  $\beta$  Zr above 862°C      CPH  $\alpha$  Zr below 862°C  
{110} planes parallel to {0001} planes  
<111> directions parallel to <1120> directions

There are six {110} planes and two <111> directions in each of the planes, hence 12 orientations of  $\alpha$  may result from a single  $\beta$  orientation.

With the electron microscope, Burgers and Van Amstel<sup>12</sup> observed that the lamellar crystallites of hexagonal close-packed zirconium form by a crystallographically reversible type of transition, and that nucleation and growth apparently do not take place in the same sense that they occur in diffusion-type phase transformation processes. Observation at high temperature of certain  $\beta$  zirconium grains revealed that the grains retained their shape on transformation to  $\alpha$  and then back again to  $\beta$  zirconium, and that after several transformations the  $\alpha$  lamellae appear in the same positions with respect to the original  $\beta$  grains that they had previously occupied.

These observations indicate that the orientation existing in recrystallized zirconium should be replaced by a new orientation when heated above the transformation temperature, and that this orientation should not be destroyed by repeated heating above and cooling below the transformation temperature. On heating above the transformation temperature the {110} $_{\beta}$  planes should form parallel to {0001} $_{\alpha}$  planes and a <111> $_{\beta}$  direction parallel to a <1120> $_{\alpha}$  direction. On retransformation of the  $\beta$  to  $\alpha$ , the old as well as entirely new orientations should appear since there are six {110} $_{\beta}$  planes and two <111> $_{\beta}$  directions parallel to which the  $\alpha$  crystallites may form. Finally, on continued heating and cooling through the transformation temperature no new orientations should appear.

a—*Transformation Texture Arising from Recrystallization Texture*: A specimen of cold-rolled Bureau of Mines zirconium was sealed in an evacuated silica capsule and heated for 1 min at 980°C and then air cooled. Diffraction photograms showing the new positions of the basal planes (compare with recrystallization photogram, Fig. 8c) are shown in Fig. 9a and b. In Fig. 6 the pole figures for the three principal planes are shown with the addition of the positions of the poles that may arise from the ideal orientation by applying Burgers' transformation mechanism.

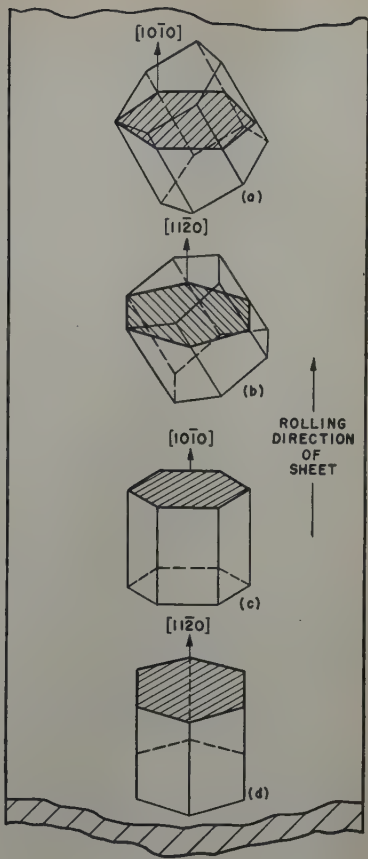


Fig. 7 — Representation of ideal preferred orientation with respect to the rolled sheet (cross-hatched plane is in rolling plane) after: a—cold-rolling, b—recrystallization after cold-rolling, c—cross-rolling, d—recrystallization after cross-rolling.

The areas marked M are the maximum intensity areas which would ordinarily be shown as the closest cross-hatched areas, and all other areas are of lesser intensity. The agreement is seen to be good when the following difficulties encountered in interpreting this set of photograms are considered:

1. The transformation orientation seems inherently possessed of more scatter than the recrystallization orientation.
2. The rings are spotty due to a much larger grain size, a condition which was not overcome by the integrating method employed.
3. There are many more orientations with consequent overlapping of scatter regions. For this reason the intensity regions of the {1010} plane pole figure of Fig. 6b are shown by dotted lines. The photograms showed very little difference in intensity around the {1010} plane rings (cf. Fig. 9a).

b—*Retention of New Texture Despite Repeated Transformation*: It has been shown that no change

Table IV. Thermal Expansivity of Zirconium in Different Sheet Directions for Various Treatments

| Condition and Type<br>of Zirconium                         | Pole Figure<br>Description,<br>Fig. No. | Coefficients of Linear Expansion<br>±0.4x10 <sup>-6</sup> per °C between 200°-300°C |                                      |              | Coefficients Cubical Exp.<br>±1.2x10 <sup>-6</sup> per °C |
|------------------------------------------------------------|-----------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------|--------------|-----------------------------------------------------------|
|                                                            |                                         | Direction of Sheet Tested                                                           |                                      |              |                                                           |
|                                                            |                                         | Thickness                                                                           | Transverse                           | Rolling      |                                                           |
| Cross rolled, recrystallized<br>(600°C), Bureau of Mines   | 5                                       | 8.7<br>(8.9)                                                                        | 5.4<br>6.3*<br>(With interferometer) | 5.4<br>6.3*) | 19.5<br>21.5                                              |
| Hot rolled (83 pct reduction at<br>760°C), Bureau of Mines | 3                                       | 7.4                                                                                 | 6.4                                  | 4.8          | 18.6                                                      |
| Hot rolled (80 pct reduction at<br>600°C), Crystal bar     | 3                                       | 8.5                                                                                 | 6.2                                  | 5.8          | 20.5                                                      |
| Transformed (heated to 980°C),<br>Bureau of Mines          | 6                                       | 6.7                                                                                 | 6.2                                  | 5.9          | 18.8                                                      |
| Cold rolled, Bureau of Mines                               | 1                                       | 10.1                                                                                | 4.8                                  | 4.6          | 20.5                                                      |
| Stress-relieved (325°C), Bureau<br>of Mines                | 1                                       | 9.3                                                                                 | 6.0                                  | 5.1          | 20.4                                                      |
| Recrystallized (600°C), Bureau<br>of Mines                 | 4                                       | 8.6                                                                                 | 6.3                                  | 5.5          | 20.4                                                      |

\* Measured in only one of the two rolling directions.

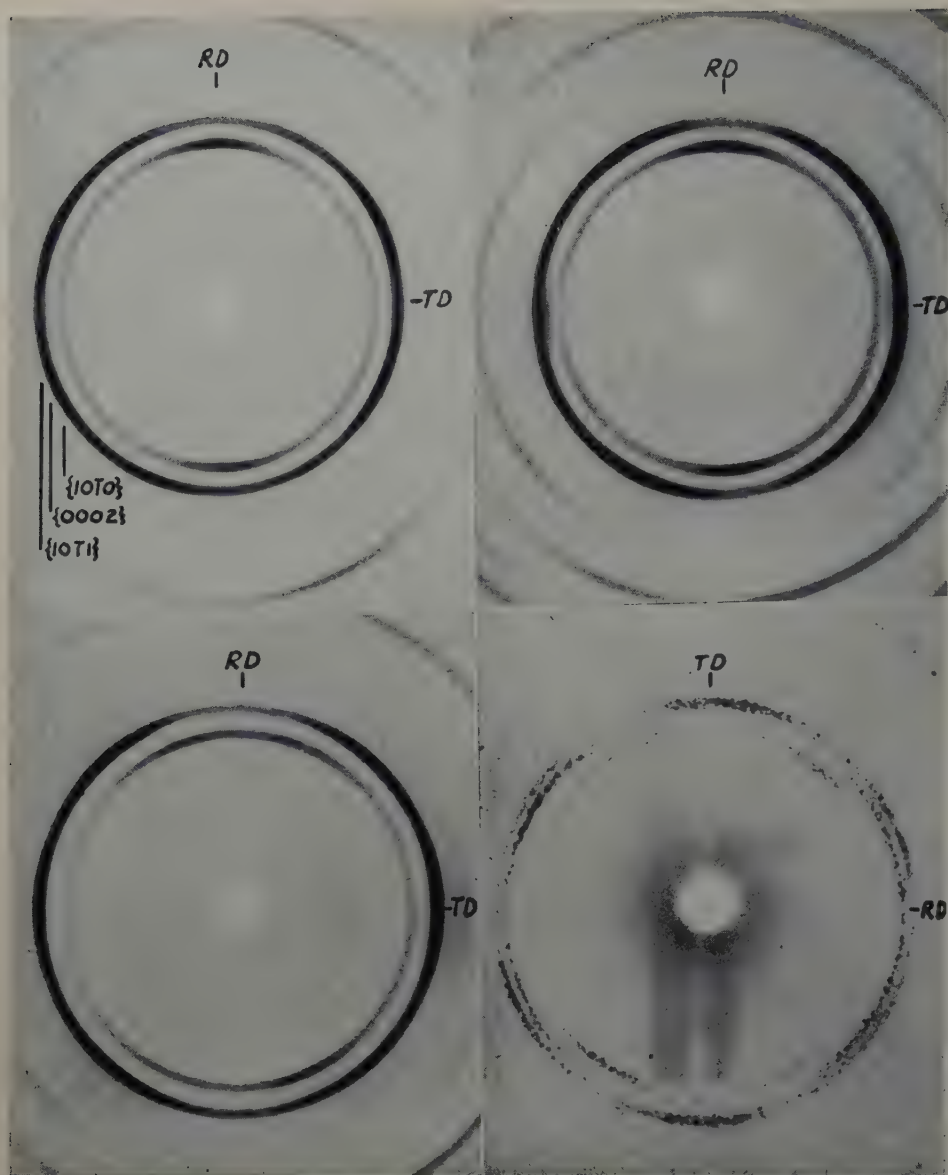


Fig. 8—Laue transmission photographs of zirconium.

- a (upper left)—Cold-rolled Bureau of Mines zirconium, 96 pct reduction. X-ray beam perpendicular to rolled sheet.
- b (upper right)—Same as a, but specimen rotated 20° about rolling direction.
- c (lower left)—Crystal bar zirconium cold rolled 95 pct reduction then recrystallized at 650°C. Beam perpendicular to rolled sheet. Specimen moving during exposure.
- d (lower right)—Same as c, but specimen rotated 75° about transverse direction.

of the transformation texture would be expected on cycling through the transformation range except such due to transformation strains and consequent noncoherent recrystallization. If, however, the mechanism were not exactly that described above but close to it, then repeated transformations would be expected to magnify the difference so that eventually a somewhat different texture or complete randomness might result. A duplicate of the specimen of Section 7a was heated eight times for a minute above the transformation temperature and water quenched after each heating. The photogram of Fig. 9b indicates that the orientation of this coarse grained specimen is entirely similar to that of the specimen of Fig. 9a which was transformed only once.

#### Anisotropy of Thermal Expansion

The available data on the expansivity of zirconium are listed in Table III. Depending on the treatment received by the material, and hence the differences in texture so produced, expansivities in the rolling direction ranging from about 4 to 6.5 microin. per in. per °C have been reported. The observed variation of expansivity with deformation and annealing treatment in Table III cannot be correlated with the X-ray results of Shinoda<sup>23</sup> who, in the temperature range 0° to 100°C, reported values of ex-

pansivity of 2.5 and 14.3 microin. per. in. parallel to the *c* and *a* axes respectively; a redetermination by X-ray methods of the expansivity revealed values of 10.3 and 4.5 microin. per in. respectively.<sup>24</sup> The correlation of the experimentally observed expansivity anisotropy with the textures described in previous sections and with values derived from X-ray observations will be discussed below.

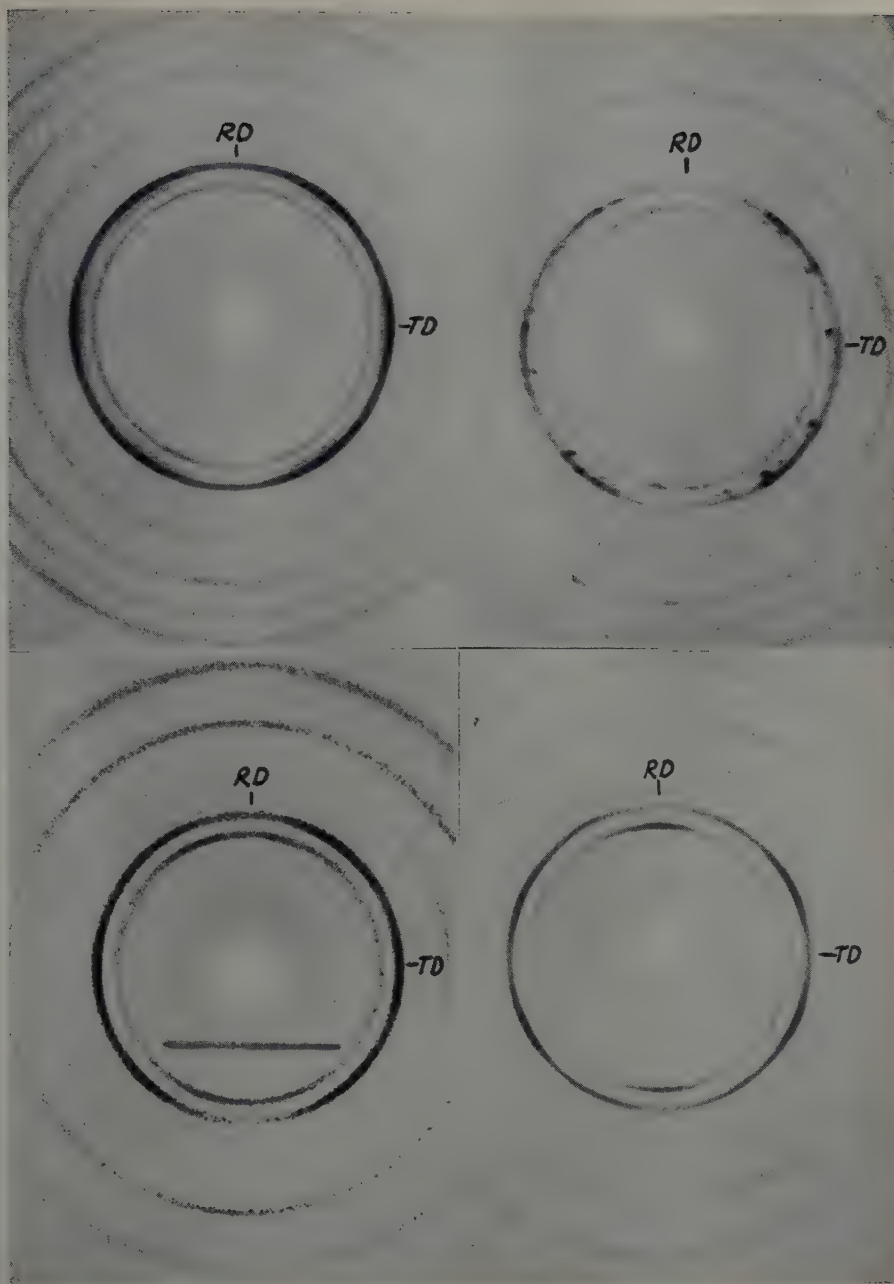
#### Experimental Technique

Expansivity was measured in the rolling, transverse, and thickness directions of rolled sheet. Most of the measurements were made by means of a quartz differential dilatometer; the dilatation strain was measured by an unbonded strain gage of about 3 microin. sensitivity. Specimens 0.3 to 0.4 in. in length were used; measurements were made in the thickness directions of rolled sheet by stacking several polished specimens to the proper depth. The specimens were heated at constant rates of 2° to 12°C per min and dilatation measurements made continuously. Results were checked in the case of a cross-rolled specimen by means of a high temperature interferometer dilatometer and were found to agree with those obtained from the differential dilatometer to within the estimated limit of accuracy,  $\pm 0.4 \times 10^{-6}$  in. per in. per °C for a 0.3-in. length of specimen. Tabulated in Table IV are the results of expansivity



Fig. 9—Laue transmission photographs of zirconium.

- a (upper left)—Cold-rolled Bureau of Mines zirconium heated to 980°C and cooled. X-ray beam perpendicular to rolled sheet. Specimen moving during exposure.
- b (upper right)—Treatment for specimen a repeated 8 times; X-ray conditions identical.
- c (lower left)—Crystal bar zirconium cold rolled 95 pct reduction and recrystallized. Beam perpendicular to rolled sheet.
- d (lower right)—Specimen of c cold rolled an additional 86 pct reduction.



measurements made on sheet with various rolling and annealing treatments.

#### Experimental Results

It is apparent that a qualitative correlation is possible between the values of expansivity listed in Table IV and the pole figures appropriate for each deformation and annealing treatment if the X-ray values of  $10.3 \times 10^{-6}$  per °C parallel to  $c$  axes and  $4.5 \times 10^{-6}$  per °C parallel to  $a$  axes are assumed for the expansivities of the unit cell axes. Thus the cross-rolled sheet, the texture of which consists of  $c$  axes scattered uniformly about the normal to the sheet direction, shows equal expansivities in the rolling and transverse directions and maximum expansivity in the thickness direction. In the case of hot-rolled and recrystallized zirconium the scatter of the  $c$  axes is principally in the transverse direction; thus the expansivity here decreases in the order thickness, transverse, and rolling direction. The transformed material exhibits  $c$  axes scattered fairly uniformly over the entire projection and correspondingly the expansivity is fairly uniform in the three sheet directions.

Expansivity measurements made on cold-rolled material showed abnormally low expansivity in the transverse direction and high expansivity in the thickness direction, considering the type of scatter for this texture. Presumably these values are abnormal because of stresses in the specimens, since on prior stress-relieving at 325°C more reasonable values for expansivity were obtained.

A more quantitative correlation of texture and expansivity is possible in the case of recrystallized sheet in which the unit cell is inclined with its  $c$  axis about 30° from the normal direction in the transverse direction. Scatter about this average orientation is fairly isotropic. The expansivities in the three sheet directions may be calculated from the formula:

$$\alpha_{th, tr, r} = (\alpha_c - \alpha_a) \cos^2 \phi_{th, tr, r} + \alpha_a$$

where  $\alpha_c = 10.4 \pm 0.5 \times 10^{-6}$  per °C  
( $c$  expansivity, Table IV)

$$\alpha_a = 4.5 \pm 0.5 \times 10^{-6} \text{ per } ^\circ\text{C}$$

( $a$  expansivity, Table IV)

$$\phi_{th, tr, r} = \text{angle between thickness (th), transverse (tr), or rolling (r) direction and mean orientation of } c \text{ axis.}$$

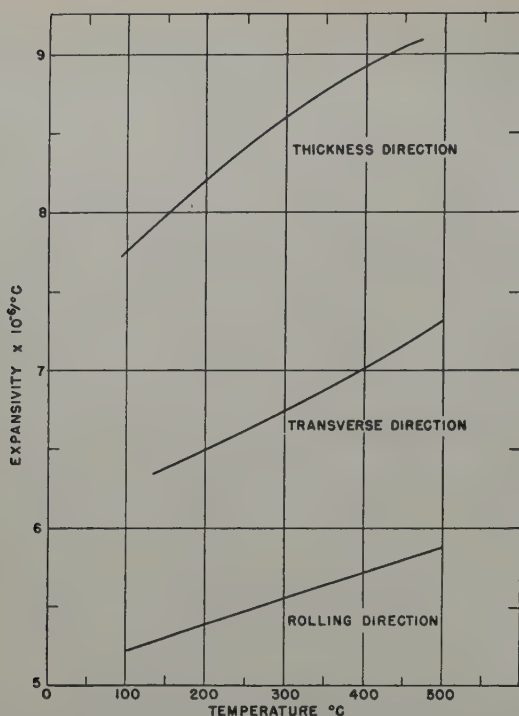


Fig. 10—Expansivity of recrystallized zirconium sheet.

The experimental and calculated expansivities for recrystallized zirconium are shown in Table V.

The uniform scatter for this texture would be expected to increase the experimental rolling direction measurement and decrease the other two measurements. Since the scatter areas of the pole figures are not quantitative no attempt was made to reconcile their resolved contributions. The variations of expansivity with temperature in the three principal sheet directions of cold-rolled and recrystallized (600°C) Bureau of Mines zirconium are shown in Fig. 10.

### Summary

1—X-ray diffraction methods were used to determine the preferred orientations of crystal bar and Bureau of Mines zirconium which were subjected to several different rolling and heating treatments. The data were presented as pole figures.

2—The cold-rolling texture indicated an average orientation that can be described as having the basal planes, {0001}, parallel to the rolling direction, but inclined from the rolling plane of the sheet about 30° in the transverse direction, with a  $\langle 10\bar{1}0 \rangle$  direction in the rolling direction.

3—The recrystallization texture was different from the cold-rolling texture. The average position of the basal planes was the same as for the cold-rolling texture but a  $\langle 11\bar{2}0 \rangle$  direction was in the rolling direction.

Table V. Linear Expansion Coefficients of Recrystallized Zr ( $\times 10^{-6}$  per °C)

|              | Thick-<br>ness Di-<br>rection | Trans-<br>verse Di-<br>rection | Roll-<br>ing Di-<br>rection | Calcu-<br>lated<br>Volume<br>Coeffi-<br>cient |
|--------------|-------------------------------|--------------------------------|-----------------------------|-----------------------------------------------|
| Experimental | $8.6 \pm 0.4$                 | $6.3 \pm 0.4$                  | $5.5 \pm 0.4$               | $20.4 \pm 1.2$                                |
| Calculated   | $8.9 \pm 0.5$                 | $7.3 \pm 0.5$                  | $4.5 \pm 0.5$               | $20.7 \pm 1.5$                                |

4—The hot-rolling texture was similar to the cold-rolling texture but with more scatter, especially in the transverse direction.

5—A specimen cross rolled at room temperature had a sharp texture with the basal planes parallel to the rolling plane and with the  $\langle 10\bar{1}0 \rangle$  direction in one rolling direction and the  $\langle 11\bar{2}0 \rangle$  direction in the other rolling direction.

6—The recrystallization texture of the cross-rolled zirconium showed the same basal plane orientation as the rolled material, but the  $\langle 11\bar{2}0 \rangle$  direction was in the  $\langle 10\bar{1}0 \rangle$  rolling direction and the  $\langle 10\bar{1}0 \rangle$  direction was in the  $\langle 11\bar{2}0 \rangle$  rolling direction.

7—The texture of surface layers of cold-rolled zirconium was found not to differ fundamentally from that of the interior of the metal.

8—Experimental evidence that the transformation mechanism of  $\beta$  body-centered cubic and hexagonal close-packed  $\alpha$  zirconium is of a crystallographically reversible nature was presented. The transformation texture indicates that the orientation relationship is the same as that reported by Burgers, namely  $\{0001\}_\alpha \parallel \{110\}_\beta, \langle 11\bar{2}0 \rangle_\alpha \parallel \langle 111 \rangle_\beta$ .

9—By X-ray diffraction the thermal expansivity of zirconium in the c-axis direction was found to be  $10.3 \pm 0.5 \times 10^{-6}$  per °C and  $4.5 \pm 0.5 \times 10^{-6}$  per °C in the a-axis direction. The thermal expansivities were measured in the thickness, transverse, and rolling directions of all sheet materials whose textures were determined, and the magnitude of expansion was found to be proportional to the degree of scatter in the three measured directions.

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# Grain-Growth and Recrystallization

## Characteristics of Zirconium

by F. J. Dunkerley, F. Pledger, V. Damiano, and J. Fulton

Grain-growth and recrystallization characteristics of a commercially pure zirconium prepared by the iodide process are reported. Grain growth from 640° to 800°C was continuous once initiated and obeyed  $D = kt^n$ . Recrystallization of zirconium occurred at temperatures of 450° to 550°C after deformations of 20 and 50 pct. Hardening from partially soluble inclusions prevented determination of the absolute rates of recrystallization, but the relative rates of recrystallization obtained are useful as a guide in fabrication practice.

**B**ASIC information needed as a guide in the hot and cold working and annealing of metals includes recrystallization and grain-growth data. A search of the literature revealed no such information for pure zirconium. This is a report of practical grain-growth and recrystallization results obtained for a commercial grade of pure zirconium on a project sponsored by the Office of Naval Research. In this work, isothermal grain-growth curves were obtained at five temperatures from 640° to 800°C inclusively; while recrystallization curves have been determined at 450°, 500°, and 550°C for the metal at the deformation levels of 20 and 50 pct. In addition to the usual variables of temperature, time, and deformation, distribution of the second phase found in all commercial grades of iodide zirconium is also treated as an important factor in these grain-growth and recrystallization studies.

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In conducting this work, two properties of zirconium were particularly pertinent in dictating experimental conditions. First, since zirconium undergoes a transformation from the  $\alpha$  close-packed hexagonal form to the  $\beta$  body-centered cubic form at 862°C, no recrystallization or grain-growth studies were made above 800°C. Second, because dissolved gases (oxygen, nitrogen and/or hydrogen) increase the hardness and lower the ductility of the solid metal, all annealing treatments in this investigation were carried out in vacuum or in a helium atmosphere.

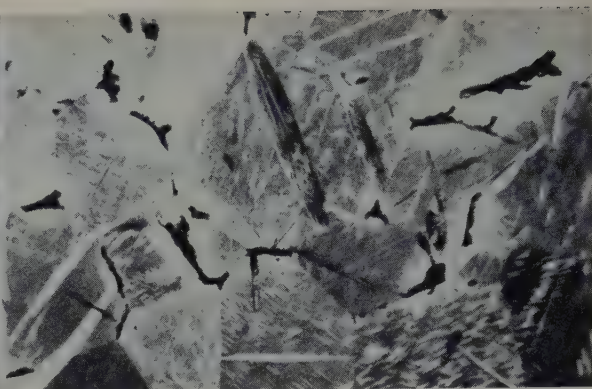
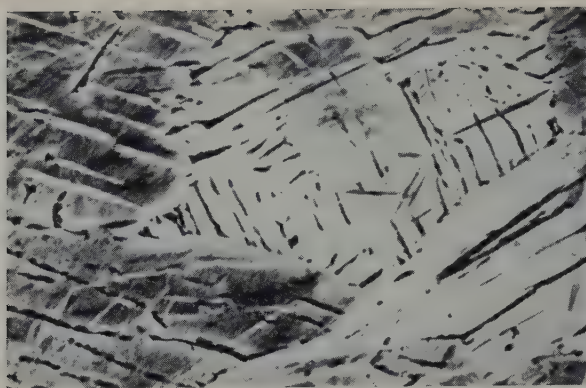
### Materials and Methods

The zirconium used in this investigation was prepared by the Foote Mineral Co. by deposition from its iodide. A spectrochemical analysis of the metal showed the following composition in weight pct: Hf, 2.1; Mg, 0.012; Fe, 0.035; Si, 0.095; Ti, 0.023; Al, 0.037; Mo, trace; Ni, trace; Cr, trace; Ca, 0.006.

Conventional metallographic procedures involving hand polishing on wet metallographic papers, followed by final polishing on fine, levigated alumina on gamal cloth and a medium speed wheel were used throughout this investigation. Grain boundaries were revealed with modified Tucker's etch containing 20 parts glycerine, 2 parts hydrofluoric acid, and one part nitric acid.

*Grain-Growth Procedure:* Three lots of zirconium, designated here as series A, B, and C were prepared for the grain-growth studies as follows:

Series A was prepared by cold swaging the ½ in. as-deposited rod to a 3/16 in. final diameter, followed



a.  $\alpha_a$  structure heated at 950° for 24 hr and air-cooled.

b.  $\alpha_b$  structure heated at 800° for 72 hr and furnace-cooled.

Fig. 1—Microstructures of deposited zirconium, swaged and heat treated. Etched with 10 pct HF in glycerine. X250.

by annealing for 20 hr at 600°C in an evacuated quartz tube for complete recrystallization. The initial grain size thus developed in the A specimens was 0.009 mm average diameter. These specimens 1/2 in. long were then sealed in vacuum in quartz tubing and heated for times varying from 1/2 to 100 hr at the temperatures 640°, 680°, 720°, 760°, and 800°C for grain-growth studies. Series B was prepared by sheathing a small section of rod with an iron pipe, hot rolling at 700°C to a 1/4 in. rod and finally cold swaging to a 3/16 in. diam rod. This stock was then heated to 800°C for 1 1/2 hr to develop a grain size of 0.024 mm. Series C was prepared by hot rolling as in the case of the B series and then annealing at 800°C to develop a grain size of 0.023 mm. The usual vacuum-annealing technique was then followed in carrying out grain-growth studies on lots B and C at the temperature levels of 640°, 720°, and 800°C. Temperatures were measured with a calibrated chromel-alumel thermocouple and were always maintained within  $\pm 1.5^\circ\text{C}$  of the values reported.

Sections both transverse and longitudinal to the swaging and/or rolling direction were examined and the grain diameters reported are the averages of those on both sections. The usual metallographic grain counting technique was used except paper negatives were made on Kodabromide enlarging paper to facilitate the grain-size measurements. Four to six areas, each containing at least 100 grains, were obtained for each specimen. Grain diameters were calculated from the formula:

$$D = \frac{1.075}{M} \sqrt{\frac{A}{n}}$$

where  $D$  is the average grain diameter in mm;  $A$ , the area of the field in sq mm;  $n$ , the total number of grains; and  $M$ , the magnification. In deriving this formula, it was assumed that all grains were regular hexagons and  $D$  was equal to the distance between opposite flats of the hexagon.

**Recrystallization Procedure:** In order to include distribution of the second phase as a variable, the stock metal was prepared and heat treated in the following manner:

The 1/2 in. deposited rod was cold swaged to 1/4 in. diam and a suitable length was sealed in an evacuated quartz tube, heated at 950°C for 24 hr, and air cooled. This produced the structure shown in Fig. 1a, designated hereafter as  $\alpha_a$ . The second phase occurs here as coarse lamellar platelets with different orientations in adjacent grains. The second section of 1/4 in. rod was heated at 800°C for 72 hr and furnace cooled.

Here the second phase is agglomerated in the grain boundaries, as shown in Fig. 1b. Material treated in this way will be designated hereafter as  $\alpha_b$ . Portions of the annealed rods were then cold worked on a 5x8 in. flat-roll mill to 20 and 50 pct reductions in cross-sectional area, light passes of about 0.005 in. each being taken to achieve as nearly uniform deformation as possible. The change in length in cold rolling was used in the usual way as the criterion of reduction in area.

Specimens of each structure and reduction were annealed isothermally in vacuum at 450°, 500°, and 550°C. A muffle furnace was used to anneal specimens for 1/2 hr or longer, while a constant temperature bath was used when the time of annealing was less than 1/2 hr. Temperature gradients in the muffle furnace were eliminated by placing the tubes in a cavity in the center of a high heat capacity steel bar, 2 1/2 in. in diam x 7 in. in length. Specimens were admitted to the furnace or salt bath at temperature in order to obtain maximum heating rate and to assure accurate time control. Time to attain temperature was experimentally found to be 2 min in the furnace and 3 sec in the salt bath, and this was subtracted from the total time of annealing in each case. The short-time specimens were heated by direct immersion in the salt bath followed by air cooling. The long-time specimens which were sealed in evacuated quartz tubes were air cooled.

Hardness measurements or the rate of softening as a result of recrystallization anneals were used as the major tool for following the progress of recrystallization, since the more classical metallographic<sup>1</sup> technique was difficult to carry out on zirconium. The annealed specimens were thus mounted in bakelite and finish-ground on 600 grit wet metallographic paper in preparation for hardness measurements. The Rockwell Superficial 30-T scale was chosen for hardness measurements because this gave the sensitivity required. An average of seven indentations on specimens reduced 20 pct, and five indentations on those reduced 50 pct were taken as the hardness of the annealed material. A limited number of metallographic determinations of percentage recrystallized were made as checks on the softening data.

## Results and Discussion

**Grain Growth:** Although not all pure metals exhibit a straight line relationship when  $\log D$  is plotted vs.  $\log t$ , as suggested by the equation<sup>2, 3</sup>  $D = kt^n$ , where  $D$  is the average grain diameter;  $k$ , a constant dependent only upon temperature;  $t$ , the



time; and  $n$ , a constant; the data obtained here conformed closely enough to this formulation to be presented in this way. On this basis, grain-growth data for zirconium, whose initial grain size is 0.009 mm at the temperature levels 640°, 680°, 720°, 760°, and 800°C, are plotted in Fig. 2. The data for 640°, 680°, and 720°C are seen to constitute a family of parallel straight lines over the entire 100 hr of the study. At 760° and 800°C, however, the growth rate shows an abrupt increase after an initial stage, and a new family of curves appears. The grain-growth data for series B and C are given in Fig. 3. Considering first the B series, it is seen that at 640°C, a long incubation period was observed, during which no noticeable change in the average grain diameter was detected. After more than 35 hr, however, grain growth began and proceeded normally. At 720° and 800°C grain growth occurred at the shortest time examined, and it is seen that the data at 640°, 720°, and 800°C form a family of straight lines (Fig. 3). A similar incubation period, followed by normal grain growth was noted for the C specimens which started at the same initial grain size. Also grain growth in this material proceeded consistently, a family of straight lines again expressing the observed behavior.

In Fig. 2, in addition to a plot of the A series, typical curves for series B at 680°C, and C at 760°C are given (there is no need for including all the B and C curves because within each series the curves are parallel). Since the initial grain size for the B and C series was much larger than that of A, the grain-growth curves for the former two series for corresponding temperatures were always shifted to a higher grain-size level. It should be noted, however, that the rate of change of  $\log D$  with  $\log t$  for series B at all temperatures is the same as in series A at 760° and 800°C, while the series C curves have a slope or rate of change of  $\log D$  with  $\log t$  intermediate between those of series A and C.

These grain-growth results very definitely reflect the effect of the second phase. Cold swaging the deposited rod caused fragmentation of the second phase, which appeared in the deposited rod as parallel platelets (with different orientations in different grains). For the A series, the subsequent recrystallization anneal caused the fine inclusion particles to spheroidize, and the structure shown in Fig. 4a resulted. Further, when the grain-growth anneals were carried out, these dispersed particles inhibited, but did not prevent, grain-boundary migration. Simultaneously, however, the small particles of second phase preferentially dissolved, and diffusion of the second-phase constituents occurred to permit the larger particles of the second phase to grow at the expense of the smaller ones. The inhibiting effect of the particles, especially as long as they remained intragranular, continued but became less effective as the size increased. Temperature, of course, had the effect of accelerating this spheroidizing process as evidenced by the fact that at 720°, 10 hr were required for agglomeration of this second phase into large angular inclusions in the grain boundaries, but within 3 hr at 800°C agglomeration was obtained (Fig. 4b).

The grain-growth curves for metal A at 640°, 680°, and 720°C and the initial part of the 760° and 800°C curves thus represent the rate of boundary migration under the inhibiting influence of the uniformly distributed second-phase particles which were simultaneously undergoing spheroidization and agglomeration. When this spheroidization proceeded to the

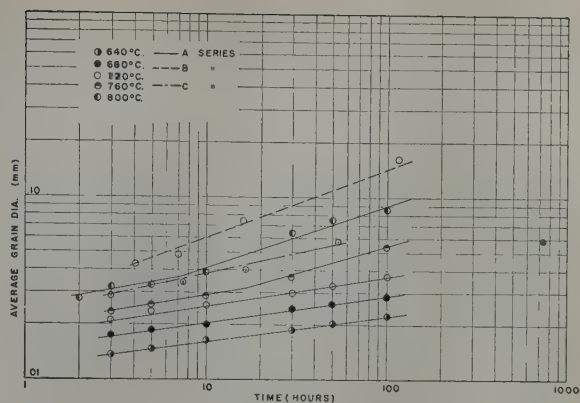


Fig. 2—Isothermal grain-growth curves for A series of zirconium at 640°, 680°, 720°, 760°, and 800°C. Curve for growth of series B, at 680°, and series C at 760°C are superimposed.

point where the intragranular particles had disappeared and large angular second-phase particles appeared in the grain boundary (but not preferentially in the dihedral angles), grain growth became much more rapid. A new family of grain-growth curves was thus obtained.

No indication of a critical temperature below which an equilibrium grain size existed, as found by Beck,<sup>2</sup> is seen in these data. Continuous grain growth in the presence of dispersed second-phase inclusions probably occurred in zirconium of this study because at all the annealing temperatures the second phase was at least partially soluble. This is qualitatively in agreement with Beck's<sup>2,3</sup> work on aluminum-manganese alloys which showed that when the second phase is soluble normal continuous grain growth occurs.

In the B series however, the second phase was initially agglomerated into large particles at grain boundaries during the recrystallization and preparation anneal as shown in Fig. 5a. At the lower temperatures, then, these particles did not have as pronounced an inhibiting effect as did the finer dispersed particles in the A material; thus a family of curves (Fig. 3) holds over the entire temperature range from 640° to 800°C, instead of only at 760° and 800°C as in series A. In the C series, the second-phase distribution was similar to that in the A series before the grain-growth anneals, except that the particles were initially larger. During the grain-growth anneals, however, these particles did not agglomerate as completely as they did in the A series. An inhibiting effect of intragranular second phase thus persisted during the entire time and at all temperatures. Consequently, the grain-growth curves for the C series are almost parallel to those of the A

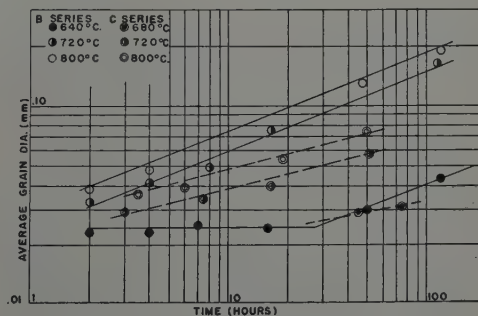


Fig. 3—Isothermal grain-growth curves for the B and C series of zirconium from 640° to 800°C.



series at 680°C, then gradually increased in slope at 720° and 800°C, but never attained the grain growth of the A and B series at 720°, 760°, and 800°C. Thus, since the same degree of agglomeration of the second phase in the grain boundaries was not accomplished in the C series as was always present in the B series

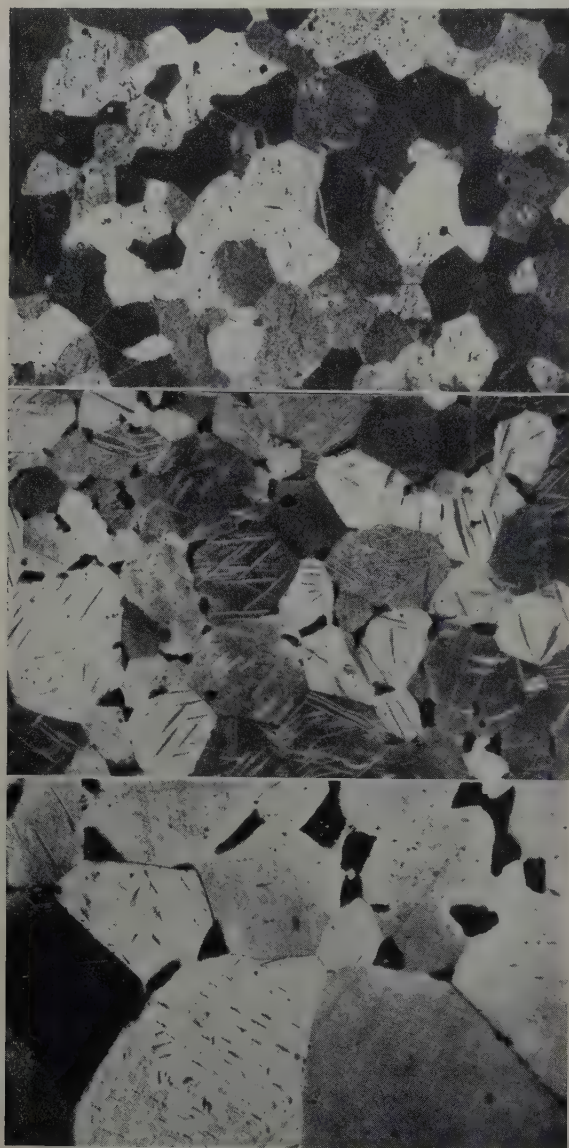


Fig. 4—Microstructures of zirconium from grain-growth studies on series A, 10 pct HF in glycerine etch. a (top)—3 hr at 720°C. X300. b (center)—3 hr at 800°C. X300. c (bottom)—50 hr at 800°C. X200.

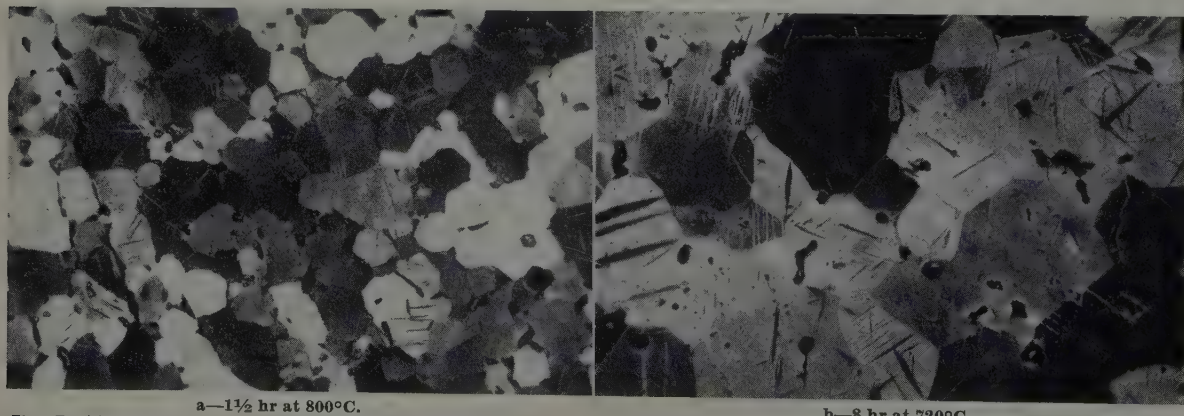


Fig. 5—Microstructures of zirconium from grain-growth studies on series B. All specimens were given the initial treatment of 1½ hr at 800°C, as shown in a. 10 pct HF in glycerine etch. X200.

throughout and in the latter stages of the A series, the inhibiting effect of the second phase gave grain-growth characteristics which were intermediate between the A and the B series.

Dispersed second-phase particles have an inhibiting effect on grain growth either directly or indirectly by obstructing the movement of atoms across grain boundaries. It is noted that, for a given constant amount of second phase, the finer the particles, the greater was the inhibiting effect. This is reasonable if it is accepted that a metal inclusion interface impedes the migration of a grain boundary, because the smaller the particle, the greater is the surface area for a constant amount of second-phase impurities. When the second phase is agglomerated in the grain boundaries, grain growth may be retarded for two reasons: 1—the actual grain boundary or interfacial area across which atoms may migrate may be decreased, or 2—changes in grain-boundary curvature accompanying growth may be prevented by the segregation of second phase in the dihedral angles. That this latter inhibiting effect was present in this work is shown by the fact that the surface of numerous A series specimens, which contained no second phase after being annealed 50 hr at 800°C, grew extremely large and very rapidly, while the internal grains in the presence of the second phase preferentially at the dihedral angles remained comparatively small. It is further noted that the surface grain boundaries are perpendicular to the surface and the dihedral angles are approximately the equilibrium value of 120°C, as predicted by Harker and Parker<sup>4</sup> and others.<sup>5</sup> Also, no additional growth of these surface grains was noted after 100 hr at 800°C, Fig. 4.

The constant slope of the series A growth curves for 640°, 680°, and 720°C establishes that  $n$ , in the expression  $D = kt^n$ , is a constant. This in turn designates that one mechanism of growth is operating at these three temperatures, and thus calculation of the energy of activation of that process can be made. This can be done by means of the relation first proposed by Arrhenius<sup>6</sup> and applied to grain growth by Burke<sup>3</sup> and others; that is, the rate of grain growth  $= Ae^{-Q_g/RT}$ , where  $A$  is a constant (independent of temperature);  $Q_g$ , the energy of activation for grain growth;  $R$ , the universal gas constant; and  $T$ , the temperature in degrees absolute. Using this equation, the energy of activation,  $Q_g$ , has been evaluated graphically for series A at 640°, 680°, and 720°C as shown in Fig. 6. The slope of this line divided by  $R$ , the universal gas constant, yields the value 68,800 cal per mol. Calculation of  $Q_g$  for the higher temperature data and for the B series from



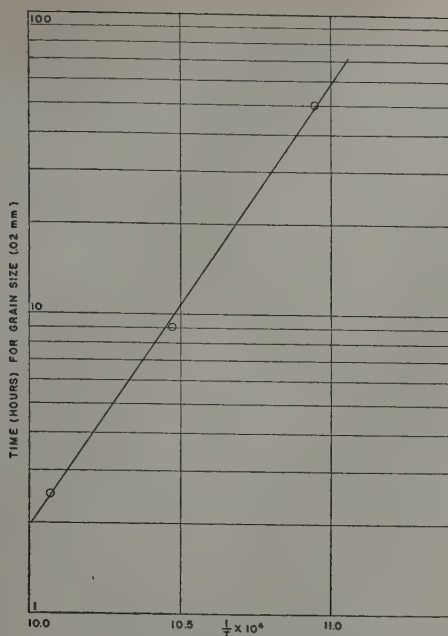


Fig. 6—Plot of time necessary to attain a grain size of 0.02 mm from an initial grain size of 0.009 mm vs. reciprocal of the corresponding absolute temperature.

680° to 720°C, inclusively, yields the value 55,000 cal per mol. These values represent the energies of activation for zirconium containing the second phase, 1—uniformly distributed, and 2—preferentially in the grain boundaries, respectively.

The incubation period in the 640°C curves of the B and C series is now being investigated more completely for zirconium over a wide range of temperatures, and these data will be reported in a later paper. Although commonly observed, present grain-growth theories neither predict nor explain the existence of an incubation or induction period for grain growth subsequent to complete recrystallization, but when a more precise mechanism is established and associated with the energetics of the process, the phenomena should be explicable.

**Recrystallization:** The isothermal softening curves obtained for zirconium for the temperatures 450°, 500°, and 550°C at 20 and 50 pct reduction levels are found in Figs. 7 and 8. It is seen that for any one distribution of second phase and amount of deformation the rate of softening is principally dependent upon temperature, increasing as the latter increases. The incubation period, however, for the metal deformed 50 pct is appreciably shorter than for zirconium deformed 20 pct. The overall rate of recrystallization increases with the amount of prior deformation. Work hardening as a result of cold work raises the initial hardness level, but the hardness difference in the fully annealed specimens may be either a result of previous annealing treatments or an effect of prior deformation on recrystallized grain size. It is unlikely that the higher final hardness is the residual effect of greater prior deformation, per se.

Definite effects of second-phase distribution and possibly solid solution can also be seen in these data. The  $\alpha_a$  form is slightly harder and appears to possess a greater capacity for work hardening than the  $\alpha_b$  form, since the hardness differential increases with deformation. This differential is maintained during annealing with the result that the shapes of the softening curves for both temperatures at the same reductions are similar. A considerably longer incubation period is required before softening begins in the

$\alpha_a$  structure than in the  $\alpha_b$ . In the  $\alpha_a$  structure, Fig. 1a, it is seen that the same phase appears as parallel platelets, and this lamellar structure has the effect of retarding softening.

Although the metallographic difficulties encountered with zirconium in the cold-worked state made it impossible to extensively use the classical metallographic approach to the study of recrystallization, some metallographic data have been obtained for correlation of hardness with percentage of recrystallization. These data yielded the correlation between hardness and the fraction recrystallized given by the relationship:

$$x^2 = 1.038 \cdot (h_o - h_x) / (h_o - h_i)$$

where,  $x$  is the percentage recrystallized;  $h_x$ , the hardness at  $x$  pct recrystallized;  $h_o$ , the cold-worked hardness; and  $h_i$ , the full-annealed hardness. This relationship holds for all but the initial phase of the softening process. This result is to be compared to that of Cook and Richards<sup>2</sup> and others<sup>6</sup> who found that pure copper obeyed the relationship of  $x = (h_o - h_x) / (h_o - h_i)$ . This latter relationship indicates that softening occurs in direct proportion to the extent of recrystallization. The relationship developed from the present data, however, indicates that softening occurs in this commercially pure grade of zirconium in direct proportion to the square of the percentage recrystallized.

This relation is believed to reflect that a diffusion process associated with and effecting a redistribution of the second phase is occurring simultaneously with recrystallization. This diffusion process continuously changed the solid-solution composition, especially in the early phases of the recrystallization anneal, and a corresponding change in hardness occurred. The hardness change resulting after the various anneal-

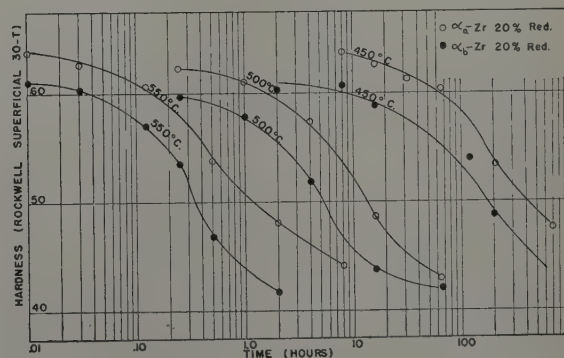


Fig. 7—Softening curves for  $\alpha_a$  and  $\alpha_b$  zirconium at 450°, 500°, and 550°C for 20 pct reduction.

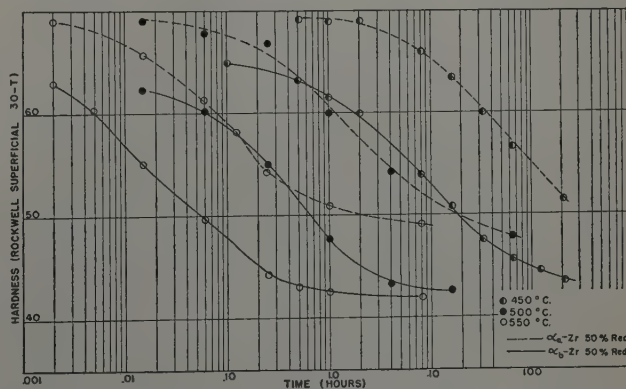


Fig. 8—Softening curves for  $\alpha_a$  and  $\alpha_b$  zirconium at 450°, 500°, and 550°C for 50 pct reduction.

ing times is thus a composite of softening resulting from recrystallization and hardening resulting from changing the composition of the continuous zirconium solid-solution phase.

Thus, since the parameter (hardness) used to follow recrystallization has also been affected by diffusion of either the second-phase components or residual oxygen in the sample tubes, the absolute rates of recrystallization of zirconium cannot be obtained from the present data. The relative rates of recrystallization revealed by these hardness measurements, however, can be used as a reliable guide to establish fabrication practice of comparable grades of pure zirconium.

No attempt is made to evaluate an energy of activation for recrystallization, since the absolute rates of recrystallization at the various temperatures cannot be ascertained. It is pertinent to point out, however, that the general shape of all the curves is similar, indicating that the same recrystallization mechanism is operative throughout and that this mechanism is independent of prior deformation and prior heat treatment.

### Conclusions

1—The isothermal grain-growth data for zirconium follows the relation:

$$D = kt^n$$

2—Second-phase inclusions have pronounced effects on grain growth.

a—In the presence of dispersed second-phase inclusions, grain growth of zirconium was retarded but growth was continuous at temperatures from 640° to 800°C.

b—The retarding effect of the second phase when agglomerated in the grain boundaries was less than when it was dispersed throughout the grains.

c—The entire elimination of the second phase resulted in accelerated grain growth.

3—The energy of activation for grain growth of zirconium in the presence of a dispersed second phase is 68,800 cal per g atom as compared with a value of 55,000 cal per g atom when the second phase is agglomerated in the grain boundaries.

4—Increasing the temperature increases the rate of recrystallization of zirconium independently of prior heat treatment and deformation.

5—The rate of recrystallization increases and the incubation period decreases with increased amount of cold work.

6—Solid solutions of oxygen or the second-phase constituent early in the recrystallization anneal increased the hardness so that appreciable recrystallization occurred before it was revealed by softening. The two structures of zirconium heat treated above and below the transformation temperature contained appreciably different distributions of the second phase, and had different recrystallization characteristics. Heat treating above the transformation temperature results in more work hardening and slightly higher hardness readings than below, and this difference persists throughout the entire anneal-

ing period. When the second phase occurs as platelets, recrystallization is retarded.

### Acknowledgment

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### DISCUSSION, D. Turnbull presiding

**H. H. Hausner and H. S. Kalish** (*Sylvania Electric Products, Inc., Bayside, L. I., N. Y.*)—We wish to congratulate the authors for their interesting paper and would like to call their attention to our paper.<sup>9</sup> The difference between the authors and our investigations lies mainly in the fact that the authors studied the recrystallization and grain growth of solid, cold-worked material, whereas we investigated the grain growth during sintering and the effect of sintering conditions on the grain size. We found an excellent correlation between grain size and the density of the respective specimen with no respect to whether this density was achieved by short-time sintering at high temperature, or by long-time sintering at lower temperatures. We found further that the grain size obtained under certain sintering conditions depends on the raw material used for the compact. The rate of grain growth was considerably greater with zirconium hydride powder than with zirconium powder used as a raw material.

**F. J. Dunkerley** (authors' reply)—The work of Dr. Hausner and Mr. Kalish on grain growth during the sintering of powdered zirconium came to our attention after this work was completed, but it is gratifying to find their results are in good agreement with our data on the wrought metal. We too noted the pronounced inhibiting effect of second-phase impurities on grain growth. In Fig. 4c micrographic evidence of accelerated growth in the absence of the second phase is shown. This phenomena is probably responsible for the more rapid grain growth noted for the zirconium hydride powder.

<sup>9</sup> H. H. Hausner, H. S. Kalish, and R. P. Angier: Powder Metallurgy of Zirconium. *JOURNAL OF METALS* (August 1951) *Trans. AIME*, pp. 625-633.

In the June 1951 issue, pp. 483 and 484, *Kinetics of Precipitation in Supercooled Solid Solutions* by G. Borelius: the illustration labeled Fig. 21, p. 483, is the illustration for Fig. 22 and belongs on p. 484, while the illustration labeled Fig. 22, p. 484, is the illustration for Fig. 21. The captions are correct as printed and remain where they are.



# Chromium-Nickel Phase Diagram

by David S. Bloom and Nicholas J. Grant

An investigation of the Cr-Ni system has revealed that there exists a eutectoid transformation at about 1180°C. The transformation in chromium implied by the eutectoid reaction was detected at about 100°C below its melting point. Associated with the eutectoid transformation, a metastable transition structure has been found.

THE Cr-Ni phase diagram is shown in current literature to be a simple eutectic system in which the high chromium end of the diagram is incompletely determined, Fig. 1. The last investigation of this system was undertaken in 1936.<sup>1</sup> Because of limitations in metal purity, especially of chromium, and temperature measuring techniques, the diagram should be accepted with some reservations, as was indicated by Hansen.<sup>2</sup> For example, the presence of the compound Cr<sub>2</sub>Ni, with a tetragonal structure,<sup>3</sup> remains unverified and incompatible with the simple eutectic diagram.

The work reported here began because of discrepancies that appeared in experimental studies in the binary alloys Cr-Ni and in the ternary system Cr-Mo-Ni. The existing binary Cr-Ni diagram failed to provide a complete explanation of observations made by microscope, X-ray, and thermal analyses.

## Experimental Methods

The materials employed were of a higher degree of purity than were available to previous investigators. The Mond nickel used had a nominal purity of 99.87 pct, while the electrolytic chromium analyzed 99.03 pct with the major impurity being 0.5 to 0.7 pct oxygen with some iron. All alloys were melted in a vacuum furnace to remove dissolved gases, sufficient carbon was added to the charge to combine with all the oxygen as CO. Final analysis determined the carbon as about 0.02 pct and the oxygen around 0.06 pct or slightly more. Stabilized zirconia crucibles and thermocouple protection tips were used throughout and contributed no detectable impurity to the melts, as long as the oxygen in the chromium was kept low. Heats averaged about 250 g, which permitted about 2 in. of the thermocouple protection tips to be submerged. The temperature drop across the thermocouple protection tip was determined to be about 3°C, a minor source of error.

The alloys, after removal from the vacuum furnace, were placed in a furnace operating in a purified argon atmosphere for the thermal analyses. An-

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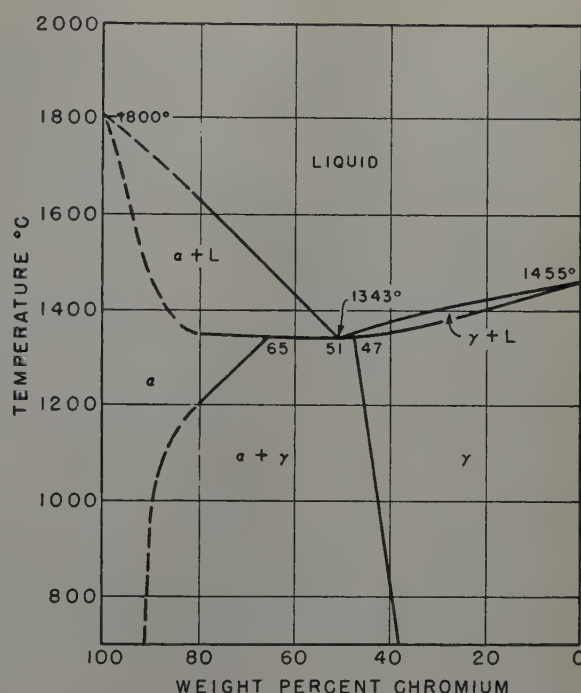


Fig. 1—Cr-Ni phase diagram drawn from the diagram in the Metals Handbook, 1948 Edition.

nealed wolfram-molybdenum thermocouples provided the primary means of temperature determination, though a Pt-Pt-10 pct Rh couple was employed for a check when possible. A sensitive, high-speed Leeds and Northrup Speedomax recording potentiometer indicated the thermocouple output.

X-ray diffraction patterns were obtained primarily on a Norelco unit, which permitted diffraction angles only up to 45° ( $2\theta = 90^\circ$ ). In general, either rotated or stationary solid samples were used, because it later evolved that many samples were susceptible to transformation resulting from the cold working involved in pulverizing. It was also noted that rotating a sample sometimes suppressed weak lines, so, usually, samples were not rotated. Later a high temperature camera was adapted for use at temperatures up to 1400°C on the Norelco unit utilizing both solid and powdered samples. Unless otherwise noted, all X-ray patterns were made with a chromium tube and a vanadium filter. Further-

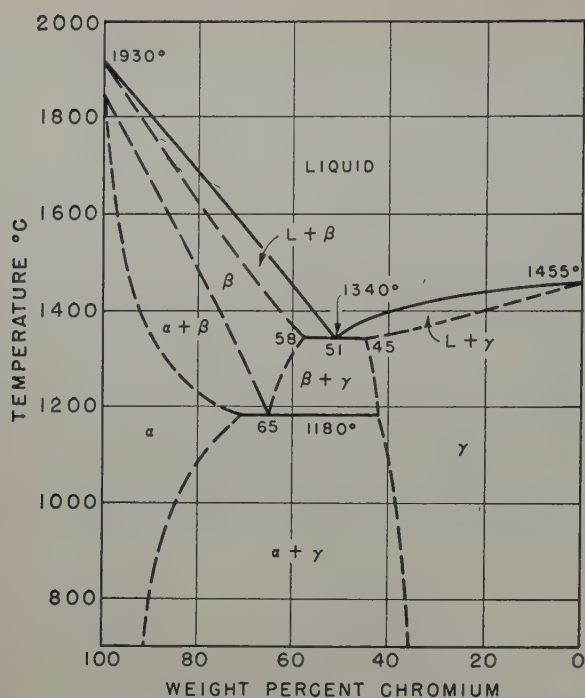


Fig. 2—Cr-Ni diagram.

more, because many samples were sensitive to mechanical polishing, practically all samples were polished and etched electrolytically. The etch generally used was a mixture of concentrated nitric acid, sulphuric acid, and phosphoric acid.

All heat treating was done in a resistance furnace in a purified-helium atmosphere. Inasmuch as the cooling rate turned out to be critical in some alloys, efforts were expended to obtain the fastest quench possible.

### Experimental Results

To facilitate the discussion of the experimental results it seems advisable to introduce here the phase diagram, Fig. 2, which resulted from this investigation. The  $\alpha$  field is the body-centered cubic chromium solid solution; the  $\gamma$  field is the face-centered cubic nickel phase, while the  $\beta$  phase is a proposed high temperature chromium structure, thought to be face-centered cubic.

In Figs. 3 through 8 are shown the as-cast microstructures of some representative alloys. Fig. 3 shows a 90 Cr-10 Ni alloy in which it can be noted that the grain boundaries do not follow the dendritic structure. This indicates that recrystallization has occurred after solidification. Fig. 4 represents an alloy of 65 Cr-35 Ni, the structure of which cannot

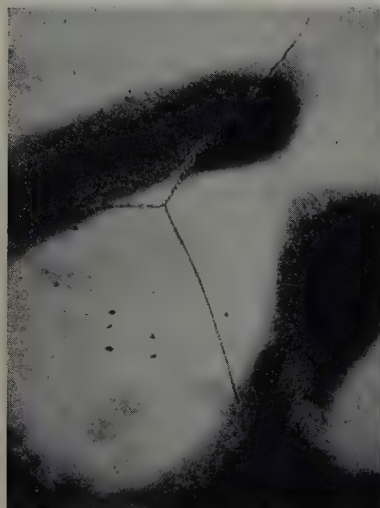


Fig. 3—90 Cr-10 Ni alloy as-cast. Light areas are chromium-rich regions. X500.



Fig. 4—65 Cr-35 Ni alloy as-cast. X150.



Fig. 5—55 Cr-45 Ni alloy as-cast. The darker regions are the chromium-rich phase. X150.

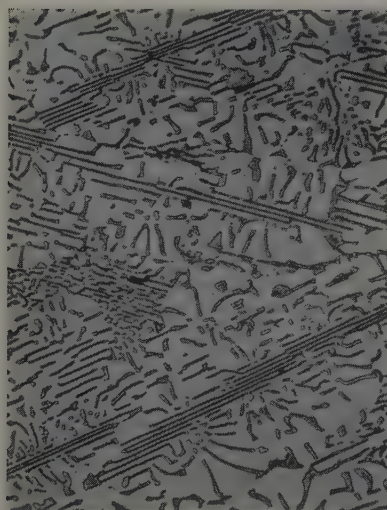


Fig. 6—51 Cr-49 Ni alloy as-cast. This is the eutectic composition. The darker regions are the chromium-rich phases. X150.

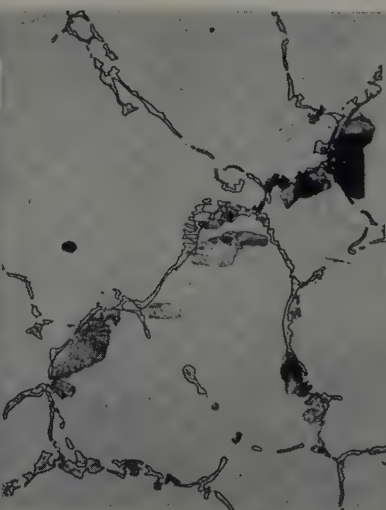


Fig. 7—45 Cr-55 Ni alloy as-cast. Light areas are the nickel solid solution, darker areas are the chromium phases. X150.

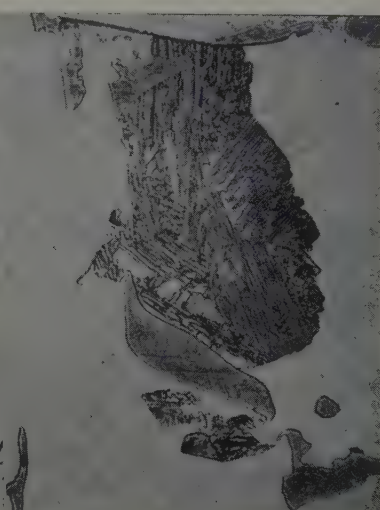


Fig. 8—45 Cr-55 Ni alloy as-cast. Light areas are the nickel solid solution, darker areas are the chromium phases. X750.





Fig. 9—Composition 60 Cr-39 Ni-1 Mo. Solution treated at 1325°C, furnace-cooled to 1150°C, held for 16 hr, then water quenched. Matrix is  $\alpha$  chromium phase, islands are  $\gamma$  nickel. X150.

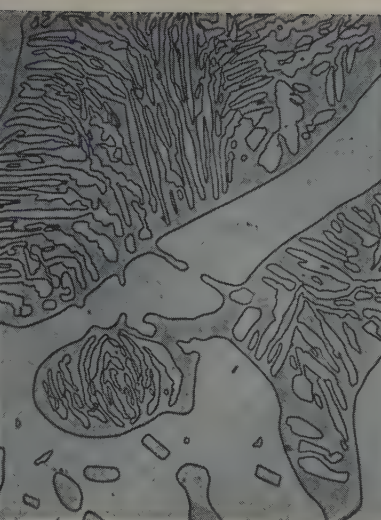


Fig. 10—Composition 55 Cr-45 Ni. Heat treatment consisted of 5 hr at 1325°C, 36 hr at 1150°C, then water quenched. Darker areas are chromium-rich phase. X150.

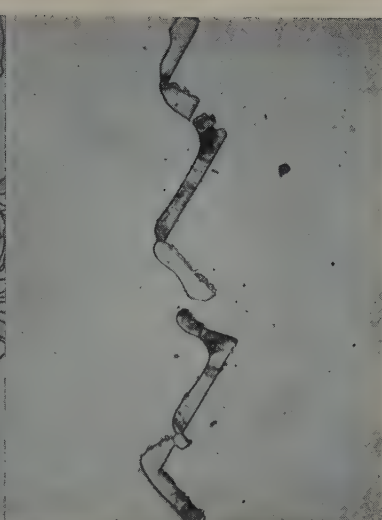


Fig. 11—Composition 45 Cr-55 Ni. Heat treatment consisted of 5 hr at 1325°C, 36 hr at 1150°C, then water quenched. X500.

be explained by the existing phase diagram. A 55 Cr-45 Ni alloy is presented in Fig. 5. It can be seen that there is a two-phase structure within the chromium-rich dendrites (the darker regions). This structure does not conform to that expected from the simple eutectic phase diagram, either. Fig. 6 reveals the structure of the eutectic composition (51 Cr-49 Ni); at a higher magnification the chromium-rich phase sometimes reveals an unanticipated internal structure. Figs. 7 and 8 show a 45 Cr-55 Ni alloy, and it will be noticed that there are three phases present. Further, at the higher magnification of Fig. 8, a eutectoid structure can be identified. From these structures alone the correctness of the simple eutectic diagram is subject to doubt.

The next series of microstructures are from specimens quenched from 1150°C, after first being solution-treated at 1325°C and furnace-cooled to 1150°C. Fig. 9 is of a 60 Cr-39 Ni-1 Mo alloy and comparing the structure with that of a 55 Cr-45 Ni alloy (Fig. 10) reveals the relation of the eutectoid structure to the eutectic structure.

A 45 Cr-55 Ni alloy is reproduced in Fig. 11 and shows the interesting form that the precipitate of the chromium-rich phase takes. Fig. 12a is the X-ray diffraction pattern corresponding to the specimen reproduced in Fig. 9, i.e., the 60 Cr-39 Ni-1 Mo alloy. The molybdenum in this alloy was inadvertently picked up from the radiation shield during melting. There was no visible difference between this alloy containing about 1 pct Mo and a similar alloy with no molybdenum, but the presence of the molybdenum permitted the retention of the high temperature phase (yet to be discussed), with no decomposition whatsoever, a condition unobtainable in a binary alloy. The apparent effect of the molybdenum was to stabilize the high temperature phase, fortunately.

There is an important difference between alloys quenched from 1250°C and those quenched from 1150°C as may be seen by comparing Figs. 13 through 15 with those just discussed. Fig. 13 is of the same alloy as shown in Fig. 9 and its X-ray diffraction pattern is shown in Fig. 12b. Comparison of Fig. 12b with Fig. 12a indicates that there is a fundamental difference between the two structures; this is also obvious from the micrographs. Fig. 14 shows the same alloy as in Fig. 10; Fig. 15 is the eutectic composition.

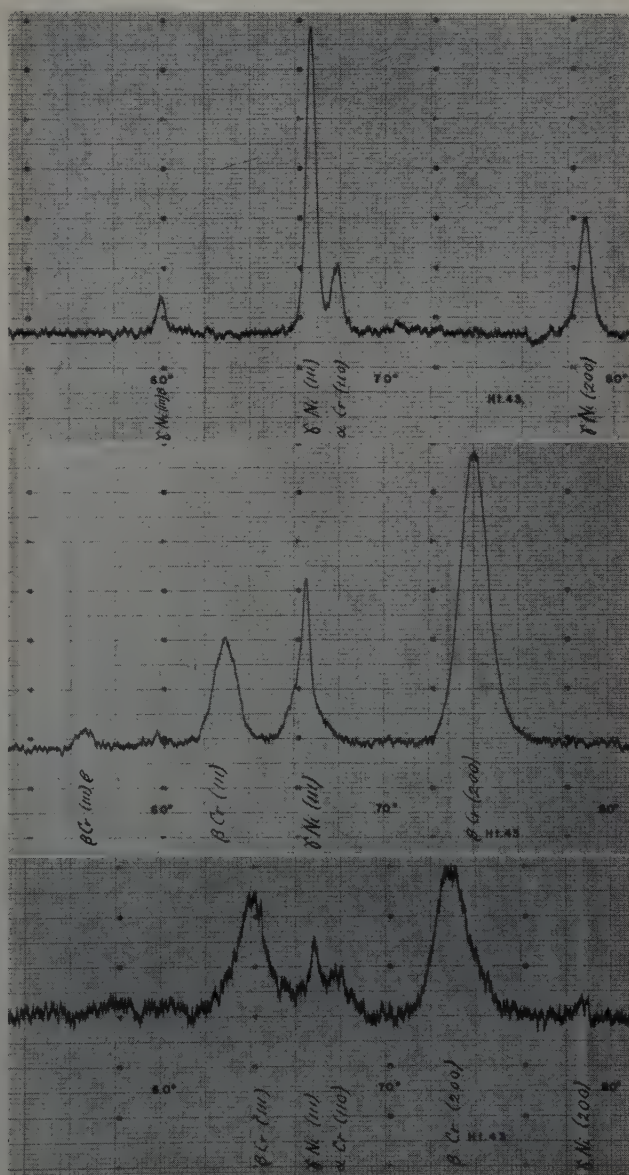


Fig. 12—X-ray diffraction pattern of 60 Cr-39 Ni-1 Mo alloy. a (top)—As-water-quenched from 1150°C. Sample not rotated so that size of lines is not representative of amount of each phase present. b (center)—As-quenched from 1250°C. c (bottom)—As-quenched from 1250°C, electrolytically polished, and then given a slight grinding on 600-grit paper.



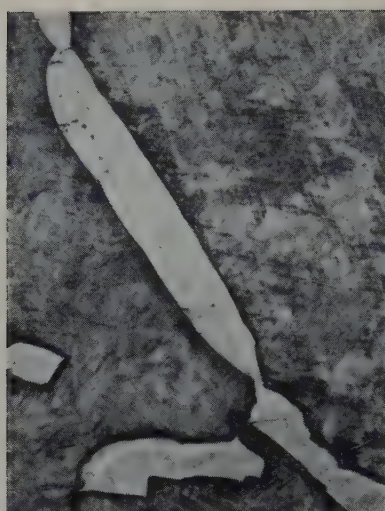


Fig. 13—Composition 60 Cr-39 Ni-1 Mo.  
Heat treatment 9 hr at 1250°C, water quenched. Light phase  $\gamma$  nickel solid solution, dark phase  $\beta$  chromium solid solution. X750.

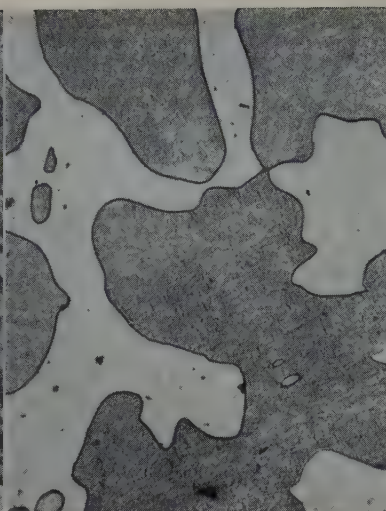


Fig. 14—55 Cr-45 Ni alloy as-quenched from 1250°C. Dark areas are the chromium-rich phase. X150.

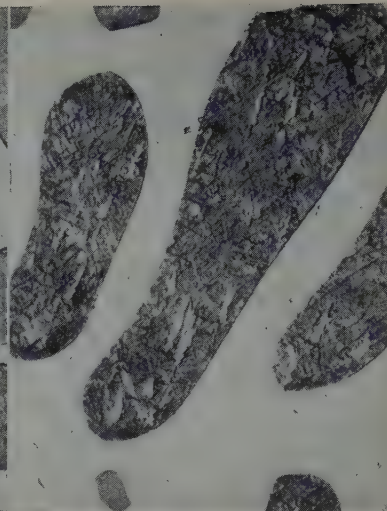


Fig. 15—51 Cr-49 Ni alloy (eutectic composition) after quenching from 1250°C. Darker areas are the chromium-rich phase. X150.

To corroborate the existence of the  $\alpha$  to  $\beta$  transformation as shown in the phase diagram, resort was made to a high temperature X-ray camera. The transformation temperature was later determined from dilatometer work to be at 1180°C. In order to

obtain all the existing lines, as it was found that solid samples did not always produce all lines, powdered samples were used. These samples were compacted and then placed in the camera, but unfortunately at the temperatures of interest these samples soon sintered into solid specimens. Further, at these temperatures the extremely large thermal gradients in the sample precluded any accurate determination of the transformation temperature.

Figs. 16a and b show that a transformation did occur at a temperature of about 1200°C. Fig. 16a shows the room temperature diffraction pattern. Fig. 16b shows the same  $2\theta$  range after the transformation has occurred. It is not possible to ascertain the crystal structure of the high temperature phase from this pattern, but it is apparent that a transformation has taken place. The absence of the  $\beta$ -Cr (111) line at about 41° ( $2\theta$ ) can be explained by the sintering of the powder compact into a solid mass.

Inasmuch as the eutectoid transformation implies a crystal transformation in pure chromium, an effort to detect this transformation was made. The transformation in chromium must take place at a temperature above 1700°C, because the specific

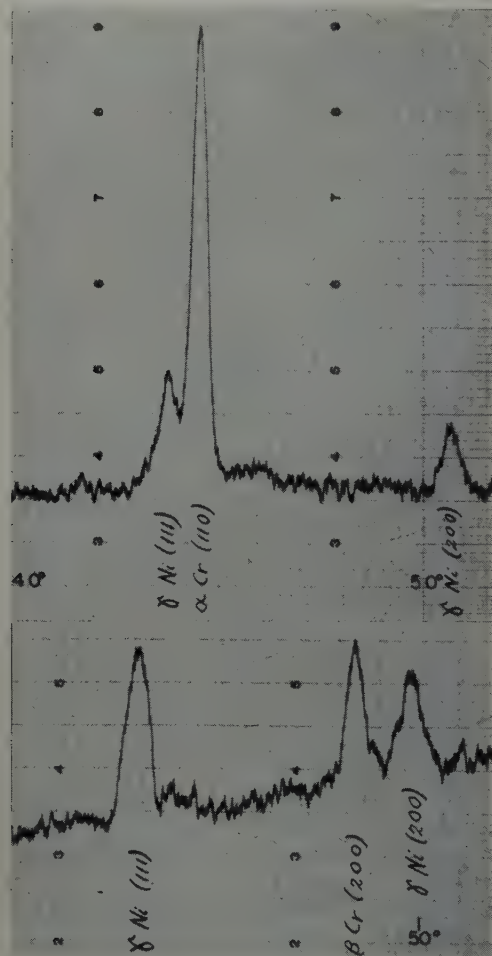


Fig. 16—X-ray diffraction patterns.  
a (upper)—Pattern taken at room temperature of 63 Cr-37 Ni alloy showing the  $\alpha$  chromium and  $\gamma$  nickel lines. Copper tube, nickel filter.  
b (lower)—Pattern taken at about 1200°C of 63 Cr-32 Ni alloy in high temperature camera. Accuracy of lines cannot be better than  $\pm 0.2^\circ$  because of shrinkage due to sintering and expansion of furnace. Comparing Fig. 16a with this figure it can be seen that the  $\gamma$  nickel lines have shifted to the left. Copper tube, nickel filter.

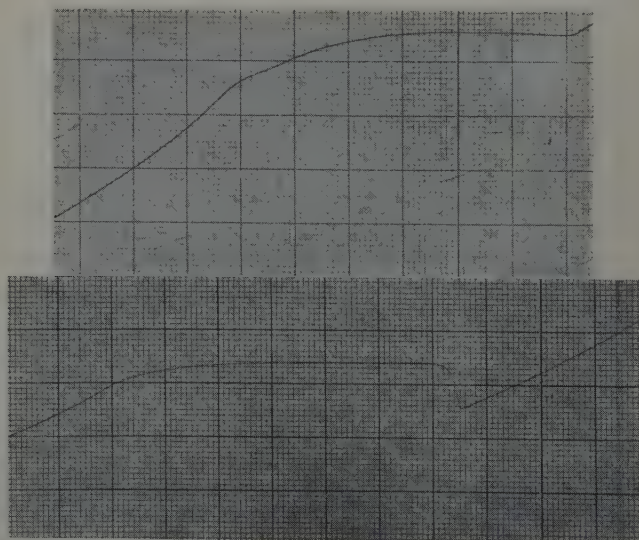


Fig. 17 a (upper)—Cooling curve of chromium. b (lower)—Cooling curve of nickel.  
Time is plotted on the abscissa from right to left, temperature is plotted on the ordinate.



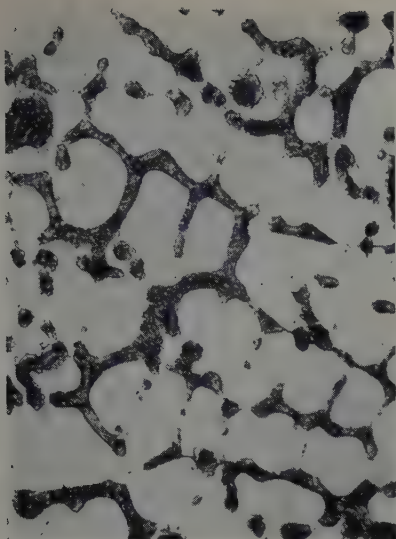


Fig. 18—90 Cr-10 Ni alloy as-drawn-up at about 1900°C into quartz tube and then quenched in water. The large round body is an oxide inclusion. X500.

resistance has been measured up to this temperature and no anomalies discovered.<sup>4</sup> However, chromium with a small amount of oxygen (1.0 pct) showed a definite discontinuity at about 1600°C, and this discontinuity was ascribed to a eutectic in the Cr-O system. Fig. 17a shows a cooling curve of pure chromium. It will be noticed that there is an unusual change of slope about 100° below the solidification temperature (more accurate values were obtained at lower cooling rates). In Fig. 17b is shown a solidification curve of pure nickel in the same apparatus under similar conditions in order to emphasize the change of slope which exists in the chromium cooling curve. Efforts to retain the high temperature phase by quenching liquid chromium were not successful; however, in Fig. 18 is shown a 90 Cr-10 Ni alloy which was quenched from the liquid. It is evident that here there are two phases present. In Fig. 3 the same alloy is shown as-slowly-cooled, and, as was mentioned before, the fact that the grain boundaries do not follow the dendritic

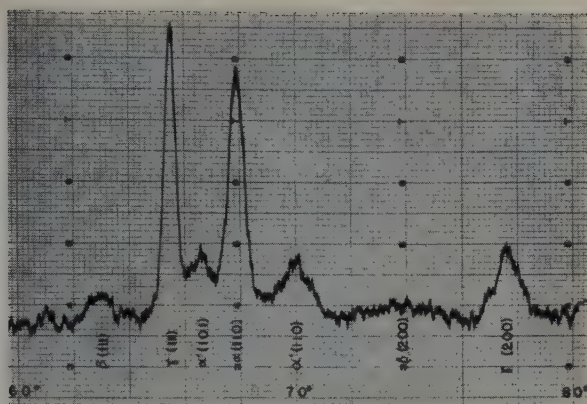


Fig. 19—65 Cr-35 Ni alloy as-quenched from 1250°C, after electropolishing only. This sample was rotating while pattern was being obtained.

structure is indicative of recrystallization after solidification.

In order to identify the high temperature  $\beta$  chromium it was necessary to use quenched specimens. It had been hoped that by employing a copper-anode X-ray tube and the high temperature camera it would be possible to find additional lines, but it seems that all higher angle lines were so diffuse at 1250°C that they were not recognizable. This same diffuseness of high angle lines was obtained when using quenched specimens in a new Norelco unit which measures  $2\theta$  values up to 150°. Consequently, only the lines present in Fig. 12b were available for study. In this connection it is of interest to note that this same diffuseness of lines in this system was reported by Jette and others in 1934.<sup>5</sup>

The available lines fit a face-centered cubic crystal with a lattice constant of 3.76 kx units; considering the metastable structure which exists, and yet to be discussed, the face-centered cubic crystal seems the most likely structure.

If the lattice constant of a face-centered cubic chromium is calculated, taking into consideration the correction in interatomic distance involved in the change in coordination number corresponding to a change from a body-centered cubic to a face-centered cubic, the result is a lattice dimension of 3.68 kx. Remembering that the face-centered cubic struc-



Fig. 20a—66 Cr-34 Ni alloy after quenching from 1250°C, metallographically polished, electrolytically etched. X500.

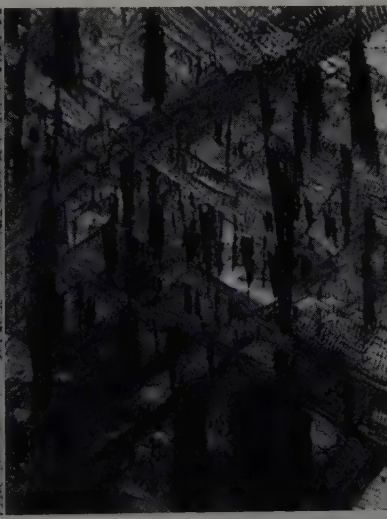


Fig. 20b—Same as Fig. 20a but with a deeper electrolytic etch. X500.

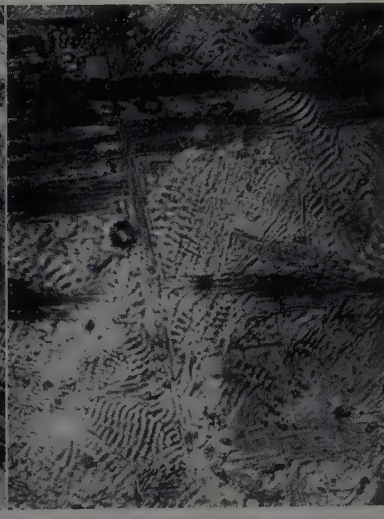
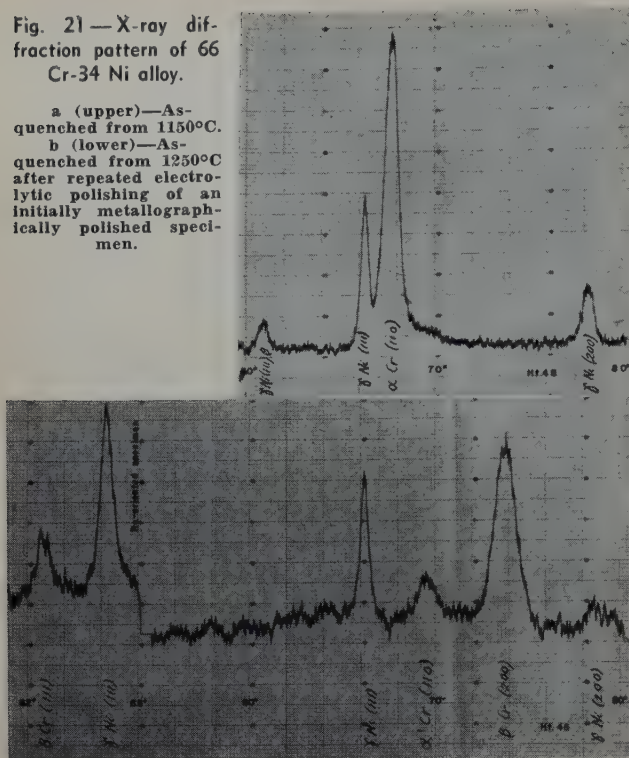


Fig. 20c—Same as Fig. 20a and b but with a still deeper electrolytic etch. X500.



Fig. 21—X-ray diffraction pattern of 66 Cr-34 Ni alloy.

a (upper)—As-quenched from 1150°C.  
b (lower)—As-quenched from 1250°C after repeated electrolytic polishing of an initially metallographically polished specimen.



ture depicted in Fig. 12b is saturated with nickel, the disparity in lattice dimensions is not too bad.

Delineation of the fields above the eutectoid temperature, while desirable, is extremely difficult because of the rapidity of quenching which is needed in order to retain the high temperature phase, particularly when in contact with the low temperature  $\alpha$ -Cr phase.

### Metastable Phase

In Fig. 19 is reproduced the diffraction pattern of a 66 Cr-34 Ni alloy as-quenched from 1250°C. In this pattern can be identified the lines due to low temperature  $\alpha$  Cr,  $\gamma$  Ni, high temperature  $\beta$  Cr, and a transition phase  $\alpha'$ . From this pattern the  $\alpha'$  phase can be tentatively identified as a body-centered tetragonal structure with an axial ratio of 1.09. However, from comparison with other patterns it has been determined that the axial ratio is not invariable. The presence of this body-centered tetragonal structure accounts for the previous report<sup>3</sup> of such a structure in this system, but the explanation offered of such a structure, that it is a compound  $\text{Cr}_2\text{Ni}$ , now appears to be incorrect.

It is interesting to note that in the similar system, Fe-C, the tetragonality of the transition structure

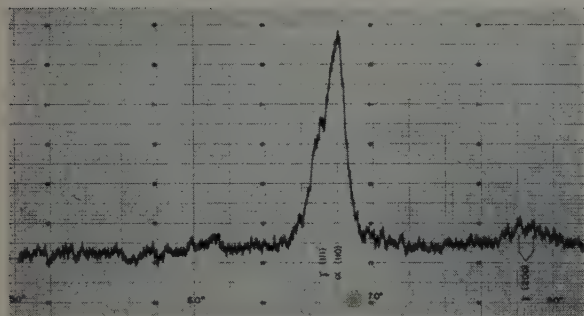


Fig. 22—65 Cr-35 Ni alloy after quenching from 1250°C, powdering, and being separated magnetically. This is magnetic portion.

(martensite) is considered to be due to the interstitially located carbon atoms; this effect cannot be presumed to be operative here.

The determination of phases is further complicated by the effect of polishing on the  $\beta$  phase and the metastable structure. Figs. 20a, b, and c are all of the 66 Cr-34 Ni composition quenched from 1250°C. This sample was first mechanically polished and lightly electrolytically etched as shown in Fig. 20a. The effect of a deeper electrolytic polish and etch of the same sample is shown in Fig. 20b. A yet deeper polish and etch resulted in Fig. 20c. It is obvious that mechanical polishing has transformed the alloy. The X-ray pattern of the alloy after repeated polishing is shown in Fig. 21b; the extra lines are due to the metastable phase which is probably a result of the mechanical work. Referring back to Fig. 20c, there is no explanation of the ripple appearing in the matrix of the specimen. Further evidence of the effect of mechanical working on the  $\beta$  phase is given in Fig. 12c, which shows the X-ray diffraction pattern of the same alloy and specimen as shown previously in Fig. 12b, except that the specimen has been polished lightly on 600-grit paper. A change in the location of the lines is evident.

Another facet of interest of the transition structure is its magnetism. If a eutectoid alloy is quenched from above the eutectoid temperature, and then powdered, portions of the powder will be rather strongly ferromagnetic. In Fig. 22 is presented the diffraction pattern of the magnetic portion of such a powder. The sample was separated by collecting the particles adhering to a small permanent magnet which had been inserted into the powder. While the pattern shows the chromium phase to predominate, there are indications of a partially formed nickel phase. The  $\gamma$  (200) line is actually comprised of two lines as confirmed by other patterns.

### Conclusions

The investigation of the Cr-Ni system has resulted in the following conclusions:

- 1—There is a transformation in chromium at about 1830°C tentatively identified as a change from a body-centered cubic to a face-centered cubic structure.
- 2—The addition of nickel lowers the transformation temperature, until at about 65 Cr-35 Ni a eutectoid temperature of about 1180°C results.
- 3—In alloys having approximately the eutectoid composition and quenched from above the eutectoid temperature, it is possible to produce a body-centered tetragonal metastable structure.

### Acknowledgment

We are grateful to the Bureau of Aeronautics, Department of the Navy, whose sponsorship made this research possible. We are also indebted to Edward LaRocca for his assistance with the high temperature X-ray camera.

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# Free Energy of Formation of Cementite And The Solubility of Cementite in Austenite

by L. S. Darken and R. W. Gurry

The solubility of cementite in austenite is computed by thermodynamic methods from the observed solubility of graphite. It is found that the solubility of cementite is greater than that of graphite in the entire austenite temperature range. Thus the prior discrepancy between this portion of the phase diagram and the observed metastability of cementite is partially resolved.

FOR several years it has been apparent that a serious discrepancy exists in certain observations pertaining to the Fe-C system. Direct experimental data indicate: 1—That the curve representing the solubility of graphite in austenite<sup>1-3</sup> crosses that for cementite<sup>4</sup> at about 945°C as shown in Fig. 1. 2—That graphite and austenite saturated therewith are stable<sup>1</sup> relative to cementite at all temperatures between the eutectoid, about 723°C, and the eutectic, about 1153°C.

These observations are mutually incompatible in view of a well-known consequence of the second law of thermodynamics, namely, that the stable phase (presumably graphite at all temperatures) has a lower solubility than the metastable phase (presumably cementite). Hence either 1 or 2 above must be in error; either the measured solubility of graphite or of cementite, or the observation as to the stability of graphite, is in error.

Our present purposes are: 1—To collate the available data on cementite and prepare a table of  $H^\circ - H_0^\circ$  and of  $(F^\circ - H_0^\circ)/T$ . This tabular method

Table I. Enthalpy and Free Energy Functions for Cementite

| °K     | $H^\circ - H_0^\circ$<br>(Cal) | $\frac{F^\circ - H_0^\circ}{T}$<br>(Cal per Deg) |
|--------|--------------------------------|--------------------------------------------------|
| 0      | 0                              | 0                                                |
| 273.16 | 3699                           |                                                  |
| 298.16 | 4329                           | 10.405                                           |
| 300    | 4376                           | 10.493                                           |
| 400    | 7023                           | 15.128                                           |
| 500    | 9952                           | 19.304                                           |
| 600    | 12746                          | 23.069                                           |
| 700    | 15452                          | 26.410                                           |
| 800    | 18248                          | 29.408                                           |
| 900    | 21073                          | 32.131                                           |
| 1000   | 23951                          | 34.627                                           |
| 1100   | 26939                          | 36.934                                           |
| 1200   | 30042                          | 39.089                                           |
| 1300   | 33165                          | 41.113                                           |
| 1400   | 36315                          | 43.020                                           |
| 1500   | 39508                          | 44.824                                           |
| 1600   | 42744                          | 46.536                                           |
| 1700   | 45970                          | 48.165                                           |
| 1800   | 49211                          | 49.718                                           |
| 1900   | 52499                          | 51.204                                           |
| 2000   | 55798                          | 52.627                                           |

seems the best and most convenient way to represent the heat and free energy of formation. 2—To determine whether the measured solubilities of cementite and graphite in austenite are in accord with the above table and the measured thermodynamic properties of austenite, in order to resolve, if possible, the existing paradox of these two solubilities.

## Enthalpy of Cementite

The enthalpy of cementite at 273°K,  $H_{273}^{\text{cem}} - H_0^{\text{cem}}$ , was computed by integration of the low temperature heat capacity as measured by Seltz, McDonald, and Wells<sup>5</sup> (68° to 298°K) and as given by the Debye functions recommended by them (0° to 68°K); the result is included in Table I. At higher temperature  $H^{\text{cem}} - H_{298}^{\text{cem}}$  is given by Kelley<sup>6</sup> who used the data of Naeser<sup>7</sup> (298° to 1037°K) and of Umino<sup>8,9</sup> (273° to 1923°K).

We have recalculated  $H^{\text{cem}} - H_{273}^{\text{cem}}$  from the data of Umino<sup>9</sup> in the following way. In the equilibrated alloy at temperature the weight fraction of cementite

is  $\frac{\text{Pct C} - \text{Pct C}^\gamma}{\text{Pct C}^{\text{cem}} - \text{Pct C}^\gamma}$ , designated  $f(C)$ , and the

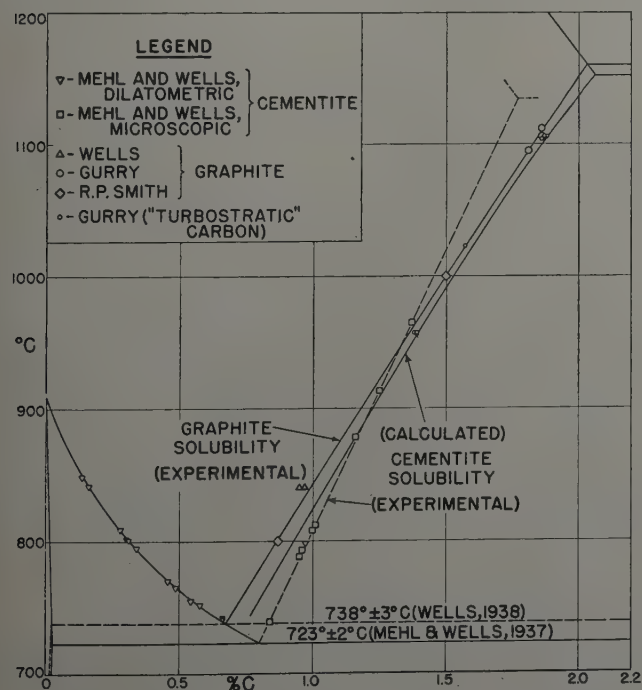


Fig. 1—Solubility of cementite and of graphite in austenite.

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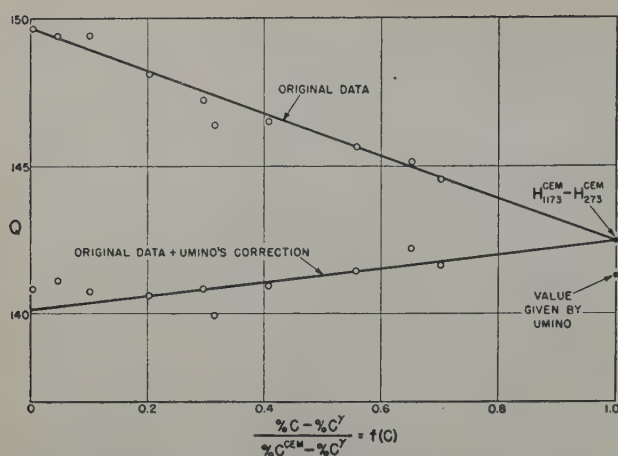


Fig. 2—Determination of the enthalpy of cementite from Umino's data on Fe-C alloys of 1.33 to 5.07 pct C equilibrated at 900°C.

weight fraction of austenite is one minus this quantity. The heat evolved on quenching 1 g of the alloy to 0°C, designated  $Q$ , is therefore:

$$Q = Q^{cem} f(C) + Q^{\gamma} [1 - f(C)]$$

where  $Q^{\gamma}$  is the heat liberated by 1 g of austenite on cooling (perhaps somewhat vague on account of the uncertainties of transformation) and  $Q^{cem}$  is  $H^{cem} - H_{273}^{cem}$ . If  $Q$  be plotted against  $f(C)$  the intercept at  $f(C) = 1$  is  $H^{cem} - H_{273}^{cem}$  and the uncertainty as to  $Q^{\gamma}$  is eliminated by the extrapolation. A typical plot is shown in Fig. 2. It will be noted that the extrapolated value is substantially independent of whether or not the correction (for austenite decomposition) suggested by Umino is used.

The results differ somewhat from those reported by Umino. It is believed that the recalculated values represent more truly Umino's experimental determinations, and these have been plotted along with Naeser's and Umino's original determinations in Fig. 3. The final curve differs only slightly from Kelley's, except in the extrapolated portion which is of no interest for the purpose of this paper, but is included in order that the results may be used at higher temperature if desired. Combination of this with  $H_{273}^{cem} - H_0^{cem}$  from the data of Seltz, McDonald, and Wells permits the evaluation of  $H^{cem} - H_0^{cem}$  over the entire range as given in Table I.

### Free Energy of Cementite

Browning, DeWitt, and Emmett<sup>10</sup> have published recently the results of their careful investigation of the equilibrium between cementite,  $\alpha$  iron, and mix-

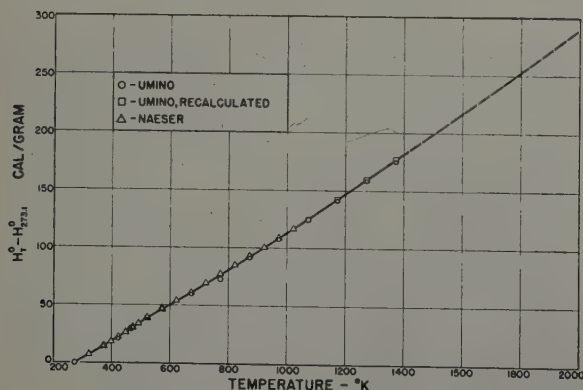


Fig. 3—Enthalpy function for cementite.

tures of methane and hydrogen in the temperature range 348° to 468°C. The results are in good agreement with the earlier investigation of Watase<sup>11</sup> (450° to 603°C) on the same equilibrium. The greatest deviation in Browning, DeWitt, and Emmett's experimentally determined equilibrium constant from a smooth curve is about 10 pct, corresponding to a precision of about 150 cal in the free energy of formation. The short temperature range gives rise to a corresponding uncertainty of perhaps 400 cal in their determination of the heat of formation of cementite.

Combination of these recent results of Browning, DeWitt, and Emmett with other information affords an opportunity for an improved evaluation of the free energy of cementite and a precise determination of the relative stability of graphite and cementite. The solubility of graphite and cementite in austenite is generally believed to be known with considerable precision in the vicinity of the eutectoid; however, preliminary calculations indicated that these data are somewhat inconsistent with the other data to be considered and hence no great weight was placed upon them here. The temperature difference (about 7°C) between the graphite eutectic and the cementite eutectic of the Fe-C system permits (in conjunction with thermodynamic data on austenite) an evaluation of the free energy of formation of cementite in the vicinity of 1153°C. The heat of

Table II. Measured Eutectic Temperatures

|                                | Cementite Eutectic Temperature, °C | Graphite Eutectic Temperature, °C | Difference, °C |
|--------------------------------|------------------------------------|-----------------------------------|----------------|
| Ruer and Goerens <sup>16</sup> | 1146                               | 1153                              | 7              |
| Kasé <sup>17</sup>             | 1151-1153*                         | 1155                              | 2-4            |
| Kasé†                          | (1130)                             | (1137)                            | 7              |

\* Rising on repetition. † White and gray irons, data obtained from cooling curves.

formation and the entropy of formation as evaluated from the low temperature heat capacity are also pertinent. These various data are collated in the following way.

The function  $\frac{F^{cem} - H_0^{cem}}{T}$  may be obtained as  $\int_0^T (H^{cem} - H_0^{cem}) d(1/T)$  or more conveniently as  $-\int_0^T \frac{H^{cem} - H_0^{cem}}{T^2} dT$ . The plot for the graphical

integration is shown in part in Fig. 4. Considerable uncertainty is involved in the low temperature portion of the integration; experimental error is greatly magnified here due to the form of the curve which, as usual, contributes a rather large area in this region. In order to eliminate this source of error at higher temperature, this error, which is a constant for temperatures above 25°C, has been represented by  $\delta$  and an asterisk has been used to denote that the integral is in error by the value of  $\delta$ . Thus,

$$\frac{F^{cem} - H_0^{cem}}{T} = \delta - \left[ \int_0^T \frac{H^{cem} - H_0^{cem}}{T^2} dT \right]^* \quad [1]$$

The free energy of formation of cementite,  $\Delta F$ , may be obtained by combining the above function with similar functions for iron<sup>12</sup> and for graphite:<sup>13</sup>



$$\frac{F^{\text{cem}} - H_0^{\text{cem}}}{T} - 3 \frac{F^{\text{Fe}} - H_0^{\text{a-Fe}}}{T} - \frac{F^{\text{gr}} - H_0^{\text{gr}}}{T} = \frac{\Delta F - \Delta H_0^\circ}{T} \quad [2]$$

Combining eqs 1 and 2:

$$\left[ \int_0^T \frac{H^{\text{cem}} - H_0^{\text{cem}}}{T^2} dT \right]^* - 3 \frac{F^{\text{Fe}} - H_0^{\text{a-Fe}}}{T} - \frac{F^{\text{gr}} - H_0^{\text{gr}}}{T} - \frac{\Delta F}{T} = - \frac{\Delta H_0^\circ}{T} - \delta \quad [3]$$

or, multiplying by  $T$  and changing signs:

$$T \left[ \int_0^T \frac{H^{\text{cem}} - H_0^{\text{cem}}}{T^2} dT \right]^* + 3 T \left( \frac{F^{\text{Fe}} - H_0^{\text{a-Fe}}}{T} \right) + T \left( \frac{F^{\text{gr}} - H_0^{\text{gr}}}{T} \right) + \Delta F = \Delta H_0^\circ + T\delta \quad [4]$$

Each of the first three terms on the left of eq 4 is now known as a function of temperature and a knowledge of  $\Delta F$  at two or more temperatures permits the evaluation of  $\Delta H_0^\circ$  and of  $\delta$ . By plotting

Table III. A Comparison of Thermodynamic Functions for the Formation of Cementite from  $\alpha$  Iron and Graphite (Cal)

|                              | $\Delta H_{298}$ | $\Delta S_{298}$ | $\Delta F_{298}$ | $\Delta F_{600}$ | $\Delta F_{800}$ | $S_{298}^{\text{cem}}$ |
|------------------------------|------------------|------------------|------------------|------------------|------------------|------------------------|
| This computation             | 5981             | 4.10             | 4760             | 2916             | 1477             | 24.92                  |
| Kelley's computation         | 5500             | 2.99             | 4610             |                  |                  | 23.8                   |
| Browning, DeWitt, and Emmett | 5453             | 3.39             | 4441             | 2850             | 1680             |                        |
| Watase                       | 5756             | 3.67             | 4661             | 2930             | 1720             |                        |
| Seltz, McDonald, and Wells   |                  |                  |                  |                  |                  | 25.7 $\pm$ 1           |
| Naeser                       | 5600             | (3.08)           | (4684)           |                  |                  | 23.9 <sup>18</sup>     |
| Roth <sup>19</sup>           | 5400 $\pm$ 1600  |                  |                  |                  |                  |                        |
| Andes <sup>20</sup>          |                  |                  |                  |                  |                  | 23.55                  |

the left side of eq 4 against  $T$  a straight line should be obtained whose intercept and slope are  $\Delta H_0^\circ$  and  $\delta$ , respectively. The plot is shown in Fig. 5. The points represent: 1—the data of Browning, DeWitt, and Emmett near the extremes of their temperature range; 2—the data of Watase near the extremes of his temperature range; 3—values obtained from the graphite and cementite solubility lines of Fig. 1\* over approximately the range covered by the investigation of Mehl and Wells;<sup>4</sup> 4—a value computed from the observation that the iron-cementite eutectic is 7°C lower than the iron-graphite eutectic;\* and 5—crude values at room temperatures from the  $\Delta H_{298}$  of Naeser<sup>14</sup> and  $\Delta S_{298}$  from the measurements of Seltz, McDonald, and Wells, and Naeser.

In constructing the line of Fig. 5, it is seen that great reliance cannot be placed on the values from the vicinity of the eutectoid of the Fe-C system, as the corresponding points lie on a curve with slope appreciably different from that drawn; nevertheless the mean value fits well. The most weight has been

\* This computation involves the use of the activity of carbon and of iron in austenite. These are taken from the work of Smith.<sup>8</sup> The equations employed are:

$$\ln a_c = \ln \frac{N_c}{N_{\text{Fe}}} + 6.6 \frac{N_c}{N_{\text{Fe}}}$$

$$\ln a_{\text{Fe}} = - \frac{N_c}{N_{\text{Fe}}} - 3.3 \left( \frac{N_c}{N_{\text{Fe}}} \right)^2$$

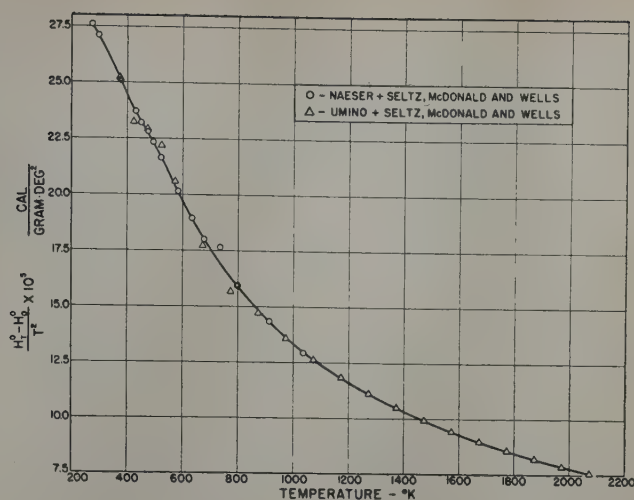


Fig. 4—Plot for evaluating the free energy function for cementite.

given: 1—the new measurements of Browning, DeWitt, and Emmett; and 2—the value from the eutectic of the Fe-C system.

Choice 2 requires some justification since the selected line of Fig. 5 implies an error of about 0.08 pct C in the graphite or cementite eutectoid (or distributed between these two points) of the generally accepted temperature-composition diagram, Fig. 1. The previously available data on the temperatures of the two eutectics were discussed by Epstein.<sup>15</sup> Only two determinations are reported in which the two eutectic temperatures were measured on the same specimen. Table II gives the results. An investigation soon to be reported by Darken and Filser of this laboratory indicates a difference of about 6° (1153° and 1147°C). Hence it is considered justifiable to conclude that this temperature difference is undoubtedly 7°  $\pm$  2°. As will appear later, a difference of 5° near 1130°C is equivalent to this selected value in so far as Table I is concerned. As a 2° error here corresponds to only 100 cal, in the ordinate of Fig. 5, this figure of 7° difference in the eutectics seems one of the most firm foundations on which to base the calculations. For this reason the line of Fig. 5 is drawn through the corresponding point (on the extreme right).

From the large scale plot from which Fig. 5 was prepared  $\Delta H_0^\circ$  is found to be 5114 cal and  $\delta = 0.952$ . This value of  $\delta$  is added to each of the integrals

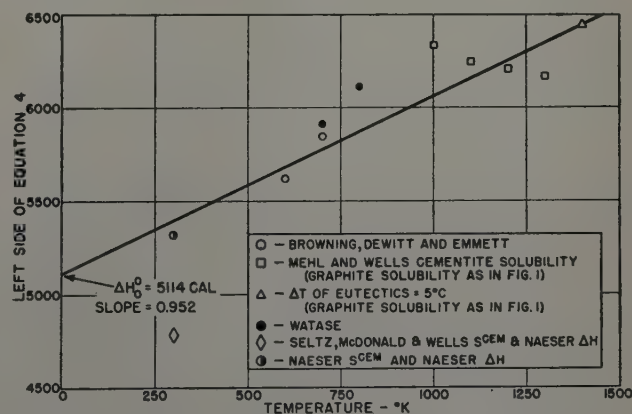


Fig. 5—Plot of a thermodynamic function pertaining to the formation of cementite, for the purpose of evaluating the error in the free energy function for cementite due to inaccuracy in the heat capacity measurements at low temperature.

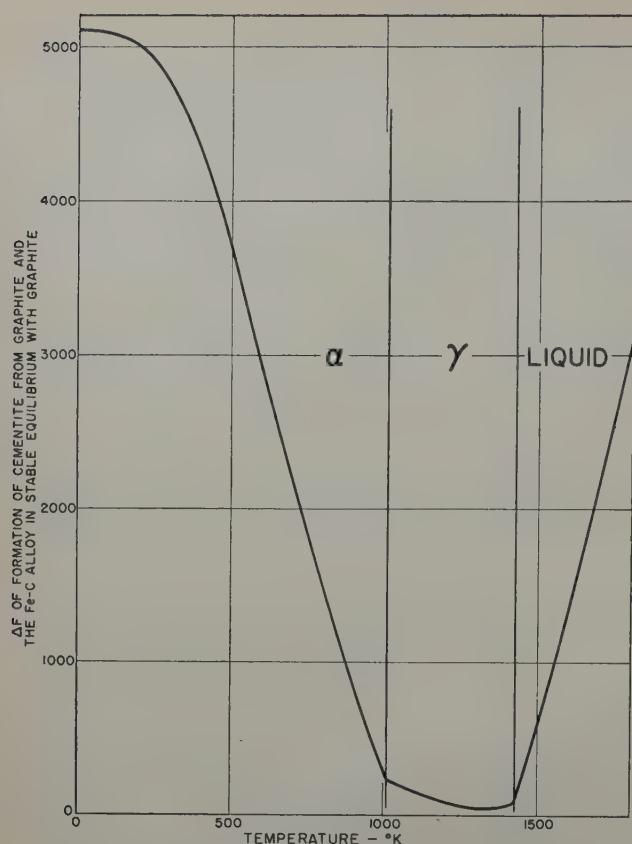


Fig. 6—Plot showing the metastability of cementite.

according to eq 1 to give  $\frac{F^{\text{cem}} - H_0^{\text{cem}}}{T}$  which is

tabulated in Table I. Of course the error  $\delta$  also implies an error in  $H^{\text{cem}} - H_0^{\text{cem}}$ . This, however, is small and no correction is made to the enthalpy table.

A comparison of various thermodynamic functions for the formation of cementite as computed from the tabular values of the free energy function (and  $\Delta H_0^\circ = 5114$ ) with those from other sources is shown in Table III. The agreement of the present computation with experiment is seen to be satisfactory in substantially all respects—a conclusion previously inferred from Fig. 5.

### Solubility of Cementite in Austenite

From the free energy function for cementite, Table I, for  $\gamma$  iron<sup>12</sup> and for graphite<sup>13</sup> the activity product  $a_c a_{\text{Fe}}$ <sup>8</sup> for equilibrium with cementite was calculated over the range of temperature from the Fe-C eutectoid to the eutectic. Combination of this with the

Table IV. Thermodynamic Functions Leading to the Solubility of Cementite in Austenite

| °K   | °C   | ΔF of Formation of Fe <sub>3</sub> C (Cal) |                                       | Observed Solubility of Graphite in Austenite, Pct C | $a_c$ in $\gamma$ Fe in Equil. Cementite <sup>‡</sup> | Calculated Solubility of Cementite in Austenite, Pct C |
|------|------|--------------------------------------------|---------------------------------------|-----------------------------------------------------|-------------------------------------------------------|--------------------------------------------------------|
|      |      | From Pure $\gamma$ Fe*                     | From $\gamma$ Fe Sat'd with Graphite† |                                                     |                                                       |                                                        |
| 1000 | 727  | + 45                                       | 244                                   | 0.64                                                | 1.14 <sub>3</sub>                                     | 0.72                                                   |
| 1100 | 827  | -183                                       | 154                                   | 0.95                                                | 1.08 <sub>3</sub>                                     | 1.01                                                   |
| 1200 | 927  | -423                                       | 88                                    | 1.27                                                | 1.04 <sub>3</sub>                                     | 1.30                                                   |
| 1300 | 1027 | -672                                       | 54                                    | 1.59                                                | 1.02 <sub>7</sub>                                     | 1.61                                                   |
| 1400 | 1127 | -926                                       | 66                                    | 1.92                                                | 1.03 <sub>2</sub>                                     | 1.96                                                   |

\* 3 Fe (pure  $\gamma$ ) + C (graphite) = Fe<sub>3</sub>C (cementite).

† 3 Fe ( $\gamma$ , saturated with graphite) + C (graphite) = Fe<sub>3</sub>C (cementite).

‡ Standard state of carbon is taken as graphite.

graphite solubility of Fig. 1 and the carbon (and iron) activity data of Smith<sup>3</sup> leads, by successive approximations, to the activity,  $a_c$ , of carbon (relative to graphite) in austenite saturated with cementite, and thus to the cementite solubility. Values of these quantities are given in Table IV. The cementite solubility thus calculated, which represents our best estimate, is shown graphically in Fig. 1. Since the activity of carbon for the austenite-cementite equilibrium always exceeds unity (the minimum value is in the vicinity of 1340°K) it is apparent that cementite is metastable over this whole range. In Fig. 6 is plotted against temperature the free energy of formation of cementite from graphite and the Fe-C alloy in stable equilibrium with graphite. Cementite is seen to be metastable in the  $\alpha$  and liquid regions as well as the  $\gamma$ .

### Summary and Conclusion

The free energy function and the enthalpy function of cementite have been computed and tabulated from data which are believed to be reliable. The table is based on enthalpy (heat content) determinations, and equilibrium determinations. Other available data are shown to agree (within the experimental error) with the tables and the value 5114 cal for  $\Delta H_0^{\text{cem}}$  (the heat of formation of cementite at 0°K). It is concluded that cementite is metastable with respect to graphite and  $\alpha$  iron from 0°K to the eutectoid and also with respect to graphite and  $\gamma$  iron saturated with graphite from the eutectoid to the eutectic. The solubility of cementite in austenite computed from the experimentally determined solubility of graphite in  $\gamma$  iron is greater than the latter over the whole temperature range. The computed values differ from the generally accepted direct experimental determinations at both limits of the temperature range covered but are in agreement with them near the center of this range.

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# Habit Phenomenon in the Martensitic Transformation

by E. S. Machlin and Morris Cohen

**G**RENINGER and Troiano<sup>1</sup> were the first to establish the fact that the habit planes of martensitic products are usually planes of high indices. In steels containing 0.55 to 1.4 pct C, the habit plane indices are  $\{225\}_A$ .<sup>\*</sup> In steels with more than 1.5 pct C and in Fe-Ni alloys, the indices are  $\{259\}_A$ . The presence of both habits in certain alloy steels has been reported recently.<sup>2</sup>

Several investigators<sup>3-6</sup> have subsequently attempted to provide an understanding of these complex habit relations. Bowles<sup>7</sup> work is the most recent and the most successful. Like Greninger and Troiano,<sup>8</sup> Bowles concluded that the transformation occurs in two steps, the first, a strain (or displacement) that is homogeneous throughout the volume of the martensitic plate, while the second is a strain that is homogeneous only within relatively small portions of the martensitic plate. The first strain yields the measured tilt of the specimen surface, but does not produce the final martensitic structure. This and the correct lattice orientations are achieved by the second strain. Bowles also reasoned that each strain could be described by the motion of a plane of no rotation and no distortion (hereinafter called the invariant plane) in a direction not necessarily contained in the plane.<sup>\*\*</sup> In applying these considerations to steels with  $\{225\}_A$  habits, Bowles found that the habit plane coincided with the invariant plane of the first strain, a result which signified that the atoms move along certain paths during the transformation. Whether this correlation results from the existence of some sort of a plate nucleus<sup>5</sup> lying along the invariant plane of the first strain, or whether the invariant plane primarily defines the

preferred directions of propagation of the first strain, will be discussed in a later section.

There are two obstacles to the general acceptance of Bowles' treatment: 1—it has not been shown that elements of his double-strain analysis are unique, and 2—it is not known whether his treatment applies to transformations yielding the  $\{259\}_A$  habit. Unless these two questions are resolved, the correlation between the habit and invariant planes in the  $\{225\}_A$  systems might be regarded as coincidental.

## Experimental Procedure

Using a 70 pct Fe-30 pct Ni alloy as an example of a  $\{259\}_A$  habit system, preliminary attempts were made to obtain a double-strain solution based on a Nishiyama<sup>\*\*\*</sup> set of orientation relations and on a Greninger-Troiano<sup>†</sup> set, adopting the stereographic technique described by Bowles<sup>5</sup> who used the Kurdjumow-Sachs<sup>††</sup> set in connection with the  $\{225\}_A$  habit. These attempts were unsuccessful because the method is essentially one of trial and error and requires either exceedingly good luck or a prior knowledge of the results being sought.

Consequently it was decided to measure independently the strain associated with the formation of a martensitic plate as well as the habit-plane indices of the particular plate. By means of matrix algebra, the measured strain was applied to the austenite lattice, whose orientation with respect to the strain was determined, in order to ascertain whether the resultant structure would have the lattice of martensite. This was not found to be the case, and hence it was assumed that the measured strain was the first of two Bowles-type strains, characterized by the motion of an invariant plane. A solution of this displacement was obtained in terms of the invariant-plane indices and the direction of motion of the atoms. Then the second strain

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\* The subscript A stands for austenite axes, and M (to be used later) stands for martensite axes.

\*\* An equivalent description of the Bowles strain is that every point moves, in a fixed direction, by an amount proportional to its original distance from a fixed plane.

\*\*\*  $(111)_A \parallel (101)_M$ ;  $[1\bar{2}1]_A \parallel [10\bar{1}]_M$ .

†  $(111)_A$  almost  $\parallel (101)_M$ ;  $[1\bar{1}0]_A$   $2\frac{1}{2}^\circ$  counterclockwise from  $[1\bar{1}\bar{1}]_M$  (looking in the direction of  $[111]_A$ ). This relationship was accurately measured by Greninger and Troiano using a single crystal of martensite of  $\{259\}_A$  habit contained in a single crystal of austenite, and is considered to be more accurate than the Nishiyama orientation relations for the purposes at hand.

††  $(111)_A \parallel (101)_M$ ;  $[1\bar{1}0] \parallel [1\bar{1}\bar{1}]_M$ .

Table I. Experimental Values of the Tangents of the Projected Angles Between the Transformed Positions of the Fiducial Markings or Axes and Their Original Positions in the Austenitic State

| Strain Matrix* | $t_{xy}^{**}$    | $t_{yz}$         | $t_{zx}$         | $t_{yx}$          | $t_{xz}$     | $t_{zy}$     | Habit of Plate***      |
|----------------|------------------|------------------|------------------|-------------------|--------------|--------------|------------------------|
| $T_{a'}$       | $+0.01 \pm 0.01$ | $+0.10 \pm 0.02$ | $-0.03 \pm 0.02$ | $-0.24 \pm 0.05$  | $0 \pm 0.01$ | $0 \pm 0.01$ | a — (592) <sub>A</sub> |
| $T_{c'}$       |                  | $+0.035$         | $+0.15 \pm 0.05$ | $+0.08 \pm 0.02$  | $0 \pm 0.01$ | $0 \pm 0.01$ | c — (295) <sub>A</sub> |
| $T_{e'}$       |                  |                  | $-0.13 \pm 0.05$ | $+0.085 \pm 0.05$ | $0 \pm 0.01$ | $0 \pm 0.01$ | e — (259) <sub>A</sub> |
| $T_{b''}$      | $+0.10 \pm 0.02$ | $-0.01 \pm 0.01$ | $-0.16 \pm 0.02$ | $-0.145 \pm 0.05$ | $0 \pm 0.01$ | $0 \pm 0.01$ | b — (529) <sub>A</sub> |
| $T_{d''}$      |                  |                  | $+0.17 \pm 0.04$ | $-0.095 \pm 0.02$ | $0 \pm 0.01$ | $0 \pm 0.01$ | d — (925) <sub>A</sub> |
| $T_{f''}$      |                  |                  | $0 \pm 0.01$     | $+0.21 \pm 0.02$  | $0 \pm 0.01$ | $0 \pm 0.01$ | f — (952) <sub>A</sub> |

\* The matrices belong to two sets distinguished by the primes. Each matrix in a set can be obtained from another in the set by a 120° rotation about  $[111]_A$ . A matrix in one set has a mirror symmetry with one other matrix in the other set across a  $\{110\}_A$  plane. All matrices are crystallographically equivalent.

\*\* The  $\pm$  values in the table represent the scatter of successive readings on a given plate. Readings for all the plates fell within this uncertainty.

\*\*\* See Fig. 2 for the orientations of these plates relative to the parent austenite.

was calculated based on the Greninger-Troiano orientation relations. Finally the elements of both strains were checked using the Bowles stereographic manipulation.

Single crystals of a 70 pct Fe-30 pct Ni alloy<sup>7</sup> were grown from the melt in a molybdenum-wound vacuum furnace using a modified Bridgman technique. Specimens were prepared with three orthogonal faces parallel to  $(111)_A$ ,  $(\bar{1}\bar{1}0)_A$  and  $(\bar{1}\bar{1}2)_A$  respectively. Polishing scratches aligned parallel to the three orthogonal axes served as fiducial markings. The crystals were then partially transformed to martensite by cooling to about  $-40^\circ\text{C}$ . Many plates were formed in a burst.<sup>7</sup>

The specimen was then set into a jig which made it possible to observe microscopically the same martensitic plate on two orthogonal faces. Thus, the habit of the plate as well as the new directions of the fiducial lines within the plate could be measured. Fig. 1 illustrates the parameters that were recorded, and Table I presents a compilation of the results.

In the interpretation of these data the correspondence between subscripts and axes is as follows:

|   |                       |
|---|-----------------------|
| X | $[\bar{1}\bar{1}2]_A$ |
| Y | $[1\bar{1}0]_A$       |
| Z | $[111]_A$             |

For example,  $t_{zx}$  is the tangent of the angular dis-

placement of a scratch parallel to the Z or  $[111]_A$  direction in the X or  $[\bar{1}\bar{1}2]_A$  direction. The tangent is positive if the positive side of the  $[111]_A$  axis moves in the  $[\bar{1}\bar{1}2]_A$  direction. It is evident from Fig. 1 that the measurements for  $t_{xy}$  and  $t_{yz}$  are made on the Z or  $(111)_A$  face, for  $t_{yz}$  and  $t_{zy}$  on the X or  $(\bar{1}\bar{1}2)_A$  face, etc. The group of six tangents for a given plate comprise the nondiagonal components of a matrix:

$$T = \begin{pmatrix} t_{xx} & t_{xy} & t_{xz} \\ t_{yx} & t_{yy} & t_{yz} \\ t_{zx} & t_{zy} & t_{zz} \end{pmatrix} \quad [1]$$

This matrix will be called a  $T$  matrix inasmuch as it is composed mainly of tangents of angles. The diagonal components  $t_{xx}$ ,  $t_{yy}$ , and  $t_{zz}$  are not tangents; however they are not necessary for this analysis and no attempt was made to measure them. It will be shown later that the  $T$  matrix is related to the coordinate-transformation matrix. (Ref. 4 contains a good résumé of the elementary steps of matrix algebra as applied to the present problem.)

Of some 40 observed plates, it was found that to each permutation of the habit-plane indices there corresponded one and only one  $T$  matrix, and vice versa. The habit planes corresponding to each of the six matrices given in Table I are shown in Fig. 2 relative to the coordinates used in this study.

### Analysis of Results

It is first necessary to establish the relationships between the experimental quantities contained in the  $T$  matrix and the components of a coordinate-transformation matrix,  $A$ . The  $A$  matrix simply relates the initial and final positions of points in the transformed region. Thus, if the initial coordinates of a point are  $x, y, z$ , its final coordinates are given by:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad [2]$$

or

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = A \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad [3]$$

The equations relating the  $T$  matrix to the required  $A$  matrix are derived in Appendix I.

If it is assumed that the transformation can be described by one homogeneous strain, then application of the measured strain to the austenite lattice should generate a body-centered cubic lattice (Fe-Ni martensite). This calculation is performed in Appendix II and the conclusion is reached there that the measured strain does not yield a body-centered cubic lattice. Hence, the single-strain concept of

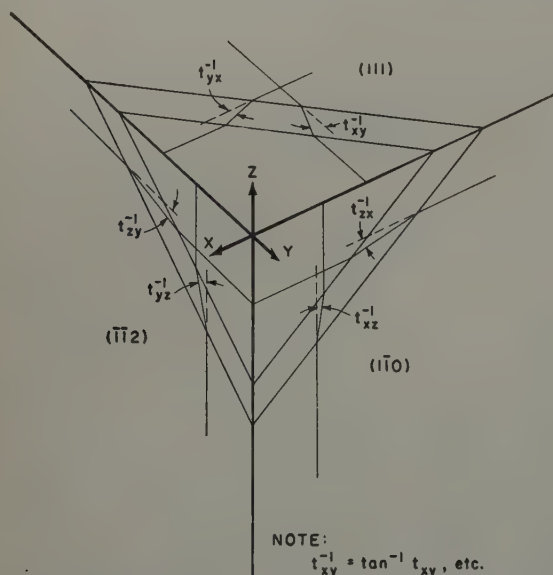


Fig. 1—Showing scribed lines the directions of which change upon traversing a martensite plate. Meaning of  $t_{xy}$ , etc. illustrated with reference to three orthogonal axes.



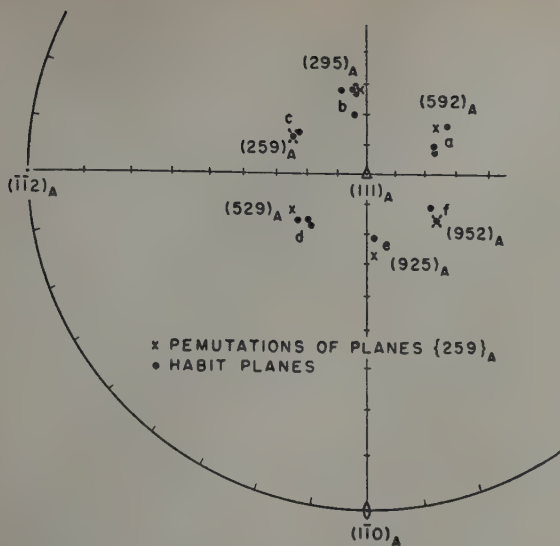


Fig. 2—Habit planes on  $(111)_A$  projection, corresponding to the six variations in Table I.

Jaswon and Wheeler<sup>4</sup> does not apply to the transformation in this alloy.

The next step in the analysis was to determine whether the Bowles double-strain method is consistent with the data. The procedure was as follows:

1—Assume that an invariant plane of general orientation with respect to the axes used in this investigation (two parameters suffice to describe the position of the pole of the invariant plane with respect to the reference axes) moves in some direction lying in the  $(111)_A$  plane.†††

2—Set up a general coordinate-transformation matrix relative to the reference axes on the basis of such motion of the invariant plane. This matrix will then contain as unknowns the two parameters that specify the position of the invariant plane relative to the reference axes, a third parameter that specifies the direction of motion of the invariant plane,†††† and a fourth parameter that specifies the magnitude of the motion. Six equations are obtained by equating‡ the nondiagonal components of the  $A$  matrix (as calculated from the measured  $T$  matrix) to the corresponding components of the general coordinate-transformation matrix. Two of these equations have already been used because of the fact that the direction of motion of the invariant plane lies in the  $(111)_A$  plane. There are four equations left and hence it is possible to calculate the parameters defining the position of the invariant plane and direction of motion of the atoms.

These calculations have been performed in Ap-

††† The direction of motion must lie in the  $(111)_A$  plane because it is found experimentally (Appendix II) that the  $(111)_A$  plane does not rotate. Hence only a single additional parameter is necessary to specify the direction of motion.

†††† This is also the direction of motion of all the atoms.

‡ This step implicitly assumes the measured strain is a homogeneous strain.

§ The fact that one and only one invariant plane is found to be associated with a given  $T$  matrix can be derived independently from the consideration that the measured  $T$  matrix really does correspond to a homogeneous strain.

¶ Indices of an invariant plane and direction of motion of atoms.

§ Knowing the positions that poles of planes and directions in the austenite take after straining to martensite (this knowledge is based on the minimum displacement hypothesis of Jaswon and Wheeler<sup>4</sup> as well as the final orientation relationships), then it is possible to check the following requirements of the Bowles analysis: 1—initial and final positions of poles of planes that contain the direction of motion of atoms during one strain must lie on the same great circle as the pole of the invariant plane of the other strain, and 2—initial and final positions of directions lying in one of the invariant planes must lie on the same great circle as the direction of the motion of atoms during the other strain.

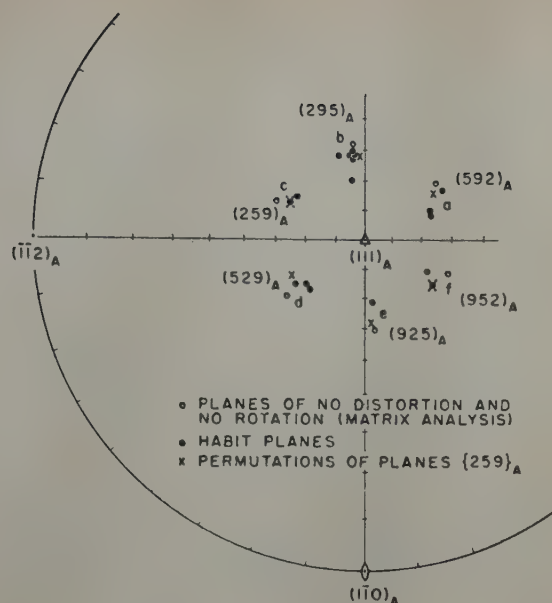


Fig. 3— $(111)_A$  projection of planes of no distortion and no rotation and corresponding habit planes.

pendix III. It is found that one and only one invariant plane is associated with a given  $T$  matrix, and that this unique invariant plane is closely parallel to the independently measured habit plane associated with the given  $T$  matrix.†† The excellent correlation between such experimental habit planes and their respective calculated invariant planes is shown in Fig. 3. The directions of atom motions for the  $T$  matrices are given stereographically in Fig. 4. Roughly these directions have the indices  $\langle 156 \rangle_A$ . In each permutation, the direction of motion does not lie in the invariant plane, and hence the first strain is not a simple shear.

Using the matrix method, the elements‡‡‡ of the second strain can be calculated from a knowledge of the first strain and the final orientation of the martensite relative to the austenite. It is assumed that the atoms move to the nearest set of proper positions in the oriented martensite lattice after the first strain.<sup>4</sup> This calculation is performed in Appendix IV. The results are shown in Fig. 5 for the case where the  $(259)_A$  permutation is the invariant plane of the first strain. The invariant plane of the second strain is close to  $(235)_M$  and the corresponding direction of motion is  $[11\bar{1}]_M$ . This direction lies in the second invariant plane, and hence the second strain is truly a shear. The elements of the first and second strains are summarized in Table II.

If the above analysis is consistent with the Bowles double-strain analysis, then the assumption of a pair of elements for either one of the strains should yield the pair of elements for the other strain using Bowles' stereographic treatments.§ Figs. 6 and 7 show that, starting with either pair of elements given in Table II, the other pair of elements can be obtained

Table II. Elements of Strains for Martensitic Transformations having  $(259)_A$  Habit

|                          | First Strain               | Second Strain   |
|--------------------------|----------------------------|-----------------|
| Invariant plane          | $(259)_A$ within $2^\circ$ | $(235)_M$       |
| Direction of atom motion | $[156]_A$ within $2^\circ$ | $[11\bar{1}]_M$ |

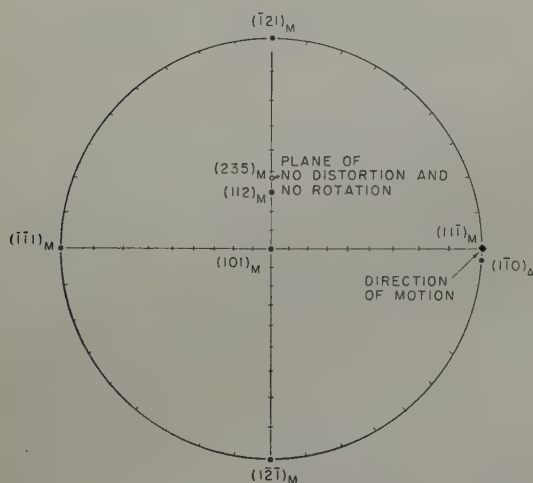
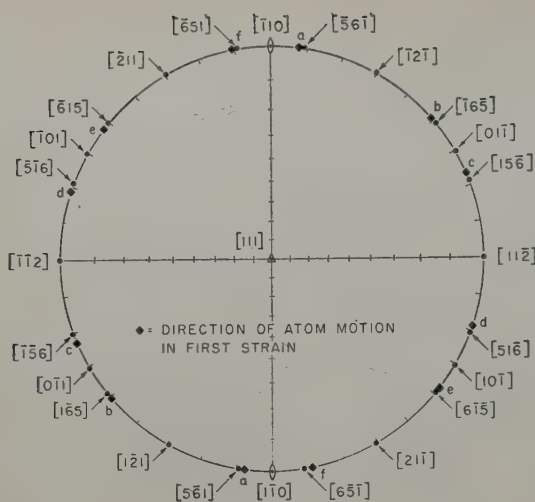


Fig. 5—Stereographic solution showing elements of second strain corresponding to (259)<sub>A</sub> habit plane.

from Bowles' stereographic method. It is interesting to note that the first invariant plane in Fig. 6 lies somewhat closer to  $(9\ 22\ 33)_A$  than to  $(259)_A$ . In evaluating these findings, it should be remembered that the probability of securing such consistent results from random choices of pairs of elements is virtually nil. From the correlation between the matrix analysis of the measured strain and the Bowles analysis, it may be concluded that the measured strain is actually homogeneous, otherwise the Bowles analysis would not yield the correct elements of the measured strain.

The matrix analysis also makes it possible to determine the succession of strains in the Bowles analysis. The sequence test performed in Appendix V demonstrates that the two strains must occur in the order already given in Table II. It is shown in Appendix V that the two strains are not commutative: if  $C$  is the final strain achieved by application

§§ This fact can be checked as follows: choose one invariant plane such that its pole lies on the great circle connecting either  $(9\ 22\ 33)_A$  and  $(235)_M$  for the  $\{259\}$  case or  $(225)_A$  and  $(112)_M$  for the  $\{225\}$  case. Choose one direction such that it lies on the great circle connecting  $[156]_A$  and  $[111]_M$  for the  $\{259\}$  case or  $[112]_A$  and  $[111]_M$  for the  $\{225\}$  case. This choice of a pair of elements will then determine the other pair of elements having internal consistency with the Bowles analysis, yet will not be the solution experimentally obtained.

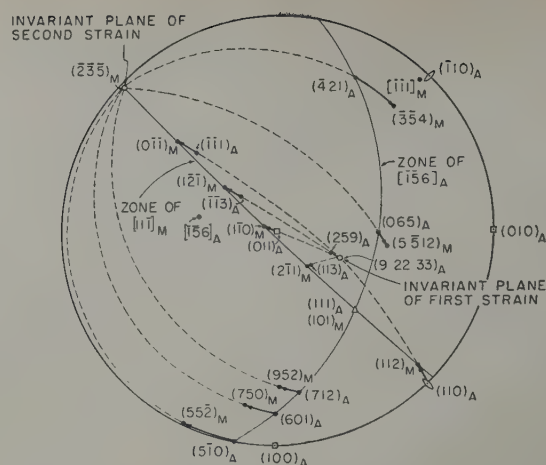


Fig. 6—Stereographic analysis of plane transformations.

**Initial and final positions of poles of planes that contain the direction of atom motion during one strain lie on the same great circle as the pole of the invariant plane of the other strain.**

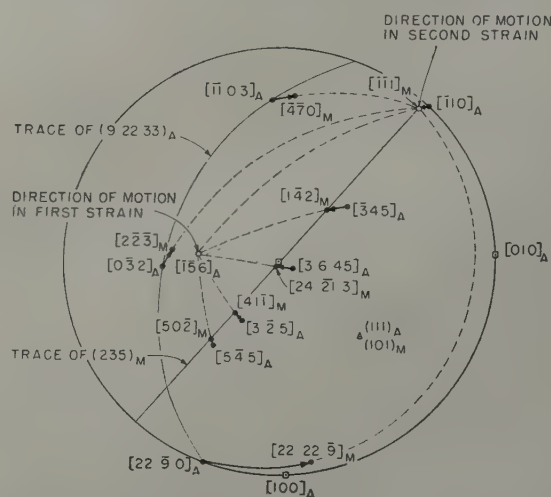


**Fig. 7—Stereographic analysis of direction transformations.**

Initial and final positions of directions lying in one of the invariant planes lie on the same great circle as the direction of atom motion during the other strain.

of A followed by B, then application of B followed by A does not result in C. Thus, the correct orientation relation cannot be attained except by the proper sequence of the invariant-plane strains in Table II.

All the results described here hold, in principle, for the  $\{225\}_A$  as well as for the  $\{259\}_A$  systems.

## Discussion of Results

*Implications of the Bowles Analysis:* The question may now be raised as to the uniqueness of the solutions obtained using the Bowles double-strain analysis: that is, does a knowledge only of the orientation relationship between the austenite and martensite lattices and their structures permit a unique prediction of the elements of the two invariant-plane strains? Consideration of this problem leads to the conclusion that the Bowles double-strain analysis, of itself, does not yield a unique pair of invariant-plane strains.<sup>§§</sup> Some additional condition is required to make the solution unique. This condition is, according to the reaction-path concept of the martensitic transformation, that the first strain involving the minimum activation energy, whether it can be predicted a priori or not, is the one that actually operates. Then, the Bowles analysis, on the basis of the final orientation relations, will predict



a unique set of elements for the second invariant-plane strain. Theoretically, if the potential energy curve as a function of the strain for each possible first strain was known, then a unique pair of invariant-plane strains, and thus their elements, could be predicted.

From the observation that the atom motion in the second strain takes place along the only direction that remains close-packed in the unrotated, but distorted  $(111)_A$  plane after the first strain, for both the  $\{225\}_A$  case and  $\{259\}_A$  case, tentative criteria for predicting the unique invariant plane of the first strain (and hence the habit plane) can be set up using the Bowles stereographic analysis and the final orientation relationship between the austenitic and martensitic structures. Of the two close-packed directions in the  $(101)_M$  plane, the direction of motion in the second strain is selected as the one which makes the smaller angle with its original close-packed  $\langle 110 \rangle_A$  direction in the  $(111)_A$  plane. Thus, poles of planes in the zone of this direction must lie on the same great circle as the pole of the invariant plane of the first strain. By choosing this direction as the second direction of atom motion in the Bowles analysis, a unique prediction for the habit plane is obtained. This procedure might be termed a modified Bowles method.

The foregoing criterion for the habit-plane prediction suggests that different orientation relations will predict different habit-plane indices. In particular, the Kurdjumow-Sachs orientation predicts the  $\{225\}_A$  set of habit plane indices, the Greninger-Troiano orientation predicts the  $\{259\}_A$  set, and the Nishiyama orientation predicts a  $\{5\ 34\ 46\}_A$  set. It should be emphasized that the above criterion for prediction of the habit plane does not mean that the habit plane is controlled physically by the final orientation relationship, rather the reverse is implied: that is, the first strain corresponding to the minimum activation energy path will, according to the criterion, uniquely determine the final orientation relationship as well as the habit plane.

**Significance of Correlation between the Habit Plane and the Invariant Plane of the First Strain:** It has now been demonstrated that the double-strain mechanism of martensite formation in ferrous alloys can lead to a plane of no distortion and no rotation in the first strain lying close to the  $\{259\}_A$  habit when the Greninger-Troiano orientation prevails, and lying close to the  $\{225\}_A$  habit when the Kurdjumow-Sachs orientation prevails. These findings strongly suggest that the double-strain mechanism is real, and that the correlation of the habit plane with the first invariant plane is most significant.

There are two possible explanations for this correlation. The first explanation, as indicated by Bowles,<sup>5</sup> assumes the existence of a two-dimensional nucleus lying along the habit plane, having roughly the final radial dimensions of the plate to form. In this picture, the plate grows in thickness in such a way as to maintain the plane of the habit as an invariant plane of the first strain.

The second explanation is based on the very reasonable assumption that the martensitic embryo is quite small compared to the final martensitic plate. Thus, it is necessary to account for the preferential propagation of the transformation along the invari-

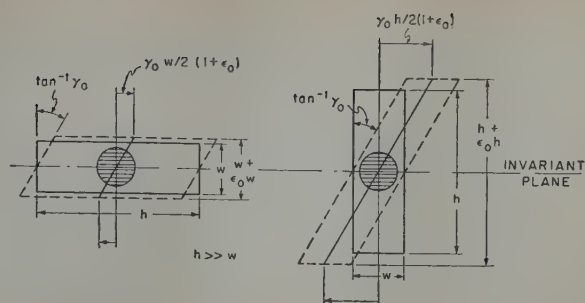


Fig. 8—Illustration of the effect of plate orientation, with respect to the invariant plane of the first strain, on strain energy.

$\gamma_0$  is the unit shear strain and  $w_0$  is the unit normal strain relative to the invariant plane. Note that if  $h \gg w$ , the displacements in the austenite surrounding the plate are smallest when the plate lies parallel to the invariant plane.

ant plane of the first strain. This result follows directly from a consideration of the strain energy developed in the austenite by a platelike region with different orientations of the plate relative to the invariant plane, as illustrated in Fig. 8. The plate has length and width dimensions  $w$ , thickness  $h$ ,

and  $\frac{w}{h}$  is taken equal to 10. From the assumption

that the stress developed at any point is proportional to the displacement of that point, and that the displacement is determined by the first strain only, the strain energy developed in the austenite for the plate lying parallel to the invariant plane turns out to be only 1/50 that for the plate lying normal to the invariant plane. Therefore, it can be concluded that as the first strain spreads out radially from the small embryo, the largest resistance is first encountered in the thickness direction. This resistance to the propagation of strain soon reaches a sufficient magnitude to limit further growth in thickness, probably by the onset of plastic flow.<sup>7</sup> The propagation of the strain along the invariant plane is relatively unhindered, and hence the plate spreads outward from the embryo mainly along the invariant plane of the first strain. The habit plane, as a result, lies parallel to the invariant plane of the first strain.

There are two implications in the latter basis for the choice of the habit plane. 1—Inasmuch as the invariant plane in this Fe-Ni alloy invariably belongs to the  $\{259\}_A$  family, then there must be a unique crystallographic first strain that is preferred to all other possible strains (such a unique crystallographic first strain is found experimentally as

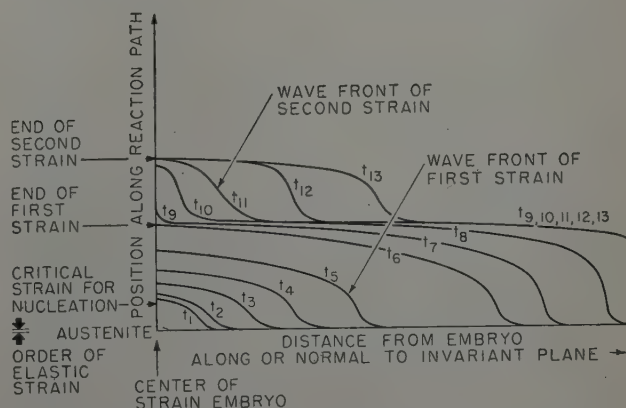


Fig. 9—Pictorial representation of propagation of first and second strain through lattice along or normal to invariant plane.

§§§ The Jaswon and Wheeler direction-transformation matrix is used for making this selection.



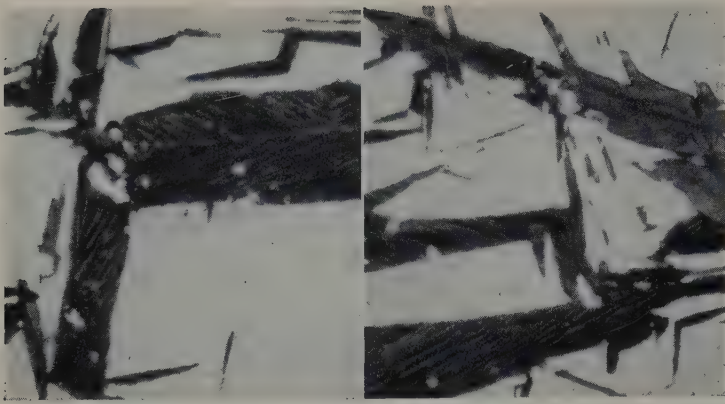


Fig. 10—Martensite plates in a 1.1 pct C, 5.4 pct Ni steel.

Transverse markings on plates appear to be the traces of the invariant planes of the second strain. X1500. Taken by W. J. Harris, Jr., M.I.T., 1948.

shown in Appendix I) and this is synonymous with a unique initial portion of a reaction path.<sup>8</sup> It is readily understandable that one reaction path would be preferred to others because the activation energy along one path is the least of all possible paths. This is the one that operates during the first strain.<sup>¶</sup> 2—The other implication of the “least resistance” basis for the choice of the habit plane is that the second strain does not contribute materially to the strain energy developed in the austenite during the time interval when the habit plane is being determined. Otherwise the strain energy would not be a minimum for a plate lying along the invariant plane of the first strain. Thus, either the homogeneous portion of the second strain must be limited to extremely small volumes so as not to affect appreciably the elastic strain energy in the surrounding austenite, or the second strain occurs after the first strain has been completed throughout the entire platelike region. The latter alternative seems improbable. The first possibility is consistent with the requirement derived from the strain measurements, that the second strain must be macroscopically heterogeneous in order not to influence the observed strains.

The mode of plate formation described as the propagation of a transformation strain outward from an embryo can be explained in terms of Fig. 9. The strain wave starts to move when the strain in the

embryo just exceeds the critical strain for nucleation. The strain at the embryo then increases as the wave front of the first strain moves away from the embryo. When the magnitude of the first strain at the embryo reaches its final value, the second strain commences. At this time, the wave front of first strain has shifted to a position somewhat removed from the strain embryo. Hence, there exists a phase lag between the wave front of the first strain and that of the second strain. After the wave front of the first strain is stopped at a barrier, the wave front of second strain catches up with it to complete the formation of a martensite plate. This model of plate formation implies that the interface region between the austenite and the martensite during formation is thicker than one atomic spacing. Bowles' model involves the addition of one plane of atoms at a time, and neglects the gradient of second strain up to and beyond the moving interface.

*Double-Strain Nature of the Martensitic Transformation:* From the fact that the habit-plane predictions of the modified Bowles method are successful, and that the invariant-plane strains must have the proper sequence to yield the correct result, it may be concluded that at any point in the transforming region the reaction actually takes place by the operation of two successive strains in point of time.<sup>¶¶</sup> This situation makes it most unlikely that the plate formation could occur via atom-by-atom diffusion across a sharp interface.<sup>9, 10</sup>

Further evidence for the double-strain mechanism is shown in Fig. 10. The subbands within the martensite are brought out by tempering an Fe-Ni-C alloy. In the case of a  $(225)_A$  habit, the structure developed by the first strain is altered during the second strain by a shear of  $(112)_M$  planes in opposite directions  $(11\bar{1})_M$  and  $(\bar{1}\bar{1}1)_M$  to form twin-bands of the martensitic structure in two variants of the Kurdjumow-Sachs orientation.<sup>¶¶¶</sup> A similar picture holds for the  $(259)_A$  habit except that unequal amounts of shear are required and the final orientations are two variants of the Greninger-Troiano set. It is believed that on tempering the carbides tend to precipitate preferentially along these twin-like boundaries, as in Fig. 10, to delineate the banded structure. Hence these subbands provide indepen-

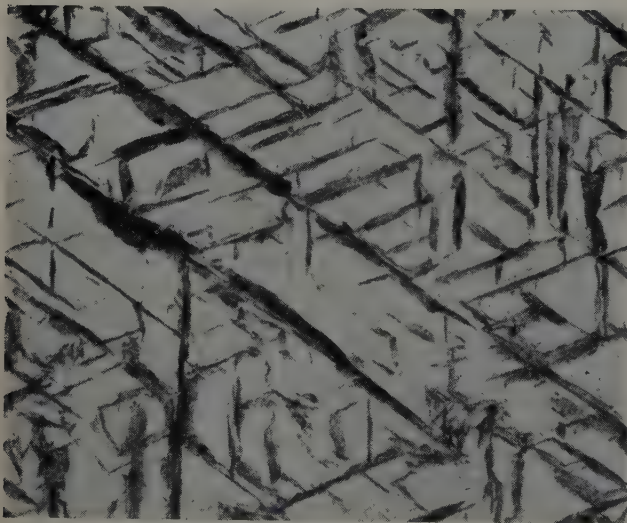


Fig. 11—Martensite plates in a medium carbon steel.

Habit plane indices are  $\{225\}_A$  and the plane of the paper is approximately  $(111)_A$ . After Greninger and Troiano.<sup>1</sup>

<sup>¶</sup> The presence of  $\{225\}$  habits as well as  $\{259\}$  habits in the same alloy system<sup>2</sup> implies the existence of two alternate reaction paths having almost the same activation energy.

<sup>¶¶</sup> There is no necessity so far to require each of these strains to be achieved by straight line motions.

<sup>¶¶¶</sup> This feature of the double-strain hypothesis is very satisfying intuitively. The first strain produces an unstable structure that is symmetrical with respect to the formation of pairs of twins through motions of  $(112)_M$  planes in the same or opposite directions. This situation does not exist until the first strain has been achieved.



dent evidence for the occurrence of a second strain that is macroscopically heterogeneous.

**Cooperative Formation of Martensitic Plates:** Because the second strain is macroscopically heterogeneous, the direction of motion of the austenite adjacent to the sides of a martensitic plate is given by the direction of motion of the atoms during the first strain. A study of the directions of motion for all the possible permutations of the  $\{259\}_A$  habit shows that there are four directions of motion lying on a cone of approximately a  $10^\circ$  half-angle about any  $\langle 110 \rangle_A$  direction; there are also six motion directions lying within a  $28^\circ$  half-angle cone about any  $\langle 111 \rangle_A$ , eight motion directions lying within a  $42^\circ$  half-angle cone about any  $\langle 100 \rangle_A$ , and twelve motion directions lying within a  $43^\circ$  half-angle cone about any  $\langle 111 \rangle_A$ . An analogous study of the directions of motion for all the possible permutations of the  $\{225\}_A$  habit indicates that there are three motion directions on a  $20^\circ$  half-angle cone about any  $\langle 111 \rangle_A$  direction; there are also four motion directions on a  $30^\circ$  half-angle cone about any  $\langle 110 \rangle_A$ , four motion directions on a  $35^\circ$  half-angle cone about any  $\langle 100 \rangle_A$ , and six motion directions within a  $55^\circ$  half-angle cone about any  $\langle 110 \rangle_A$ .

It may be expected that the strain energy per unit thickness of plate generated by the formation of plates adjoining the same austenitic region will be less if the plates tend to move the intervening austenite in the same direction rather than in opposing directions. In other words, a cooperative action in the martensitic transformation of many plates is predicted if their almost simultaneous appearance helps minimize the resisting strain energy. A rough measure of this cooperation is the number of "common" directions of motion in the first strain, and a comparison of the  $\{259\}_A$  and  $\{225\}_A$  habits shows that the degree of cooperation expected in the former is about twice that in the latter. The fact that there are twice as many  $\{259\}_A$  planes as  $\{225\}_A$  planes leads to a similar conclusion.

Pictorial evidence for this measure of cooperation is given in Figs. 11 and 12. Fig. 11, taken from ref. 1, shows a  $(111)_A$  plane in a medium carbon steel having a  $\{225\}_A$  habit. The triangular configurations of martensitic plates correspond to the three  $\{225\}_A$  poles lying on about a  $20^\circ$  half-angle cone around the  $[111]_A$  direction. This is the most preferred grouping of plates in the  $\{225\}_A$  system according to the above concept of cooperative movements. Fig. 12 shows two  $\{259\}$  type plates; specifically the habit planes are  $(5\bar{9}2)_A$  and  $(952)_A$  where the plane of the page is  $(111)_A$ . The common direction of motion (the half angle is about  $10^\circ$ ) is  $[110]_A$ . This is one of the two most preferred groupings for the  $\{259\}_A$  habit systems according to the above criterion of cooperation.

These concepts receive further confirmation in that they account for the observation of Greninger and Troiano<sup>1</sup> regarding the tendency for  $\{225\}_A$  systems to show obtuse angles between pairs of adjoining plates, whereas the  $\{259\}_A$  systems are characterized by acute angles between such pairs of plates. It turns out that a random section through the  $\{225\}_A$  grouping in Fig. 11 will exhibit obtuse angles, while a random section through the  $\{259\}_A$  grouping in Fig. 12 will exhibit acute angles.

**Twinning and the Martensitic Transformation:** Bowles<sup>5</sup> describes the elements of the two strains in the  $\{225\}_A$  system as close to those of twinning in



Fig. 12—Martensite plates in a 70 pct Fe-30 pct Ni alloy. Habit plane indices are  $\{259\}_A$  and the plane of the paper is  $(111)_A$ . X500.

the austenite and martensite respectively. In this study, it is found that the first strain has nothing in common with the twinning crystallography of austenite, whereas the second strain involves an approximation of the twinning elements for the martensitic phase. The second invariant plane is about  $5^\circ$  from the twinning plane of martensite, while the direction of atom motion is the same as in twinning.

Reinvestigation of the results of Bowles as well as those of Greninger and Troiano<sup>8</sup> discloses that the first direction of motion is in the anti-twinning direction. Thus the first strain of the Bowles  $\{225\}_A$  solution is not one of twinning in the austenitic phase. The second strain for the  $\{225\}_A$  case involves exactly the twinning elements of the martensitic phase. These facts lend credence to the conclusion that the second strain follows the first in any unit of volume undergoing the transformation. The first strain can be said to involve the most favorable reaction path for the transformation in the austenitic structure. The second strain involves the most favorable reaction path in the martensitic structure for the final position along the first strain. Indeed, it now appears that the final position along the first strain is a result of the intercession of a change in the reaction path (the second strain) which is more favorable than a continuation of the first strain.

**Magnitude of Strains:** It is interesting to note that the magnitudes of the strains associated with the transformation are much larger than elastic strains. For example, the component of strain normal to the invariant plane of the first strain is about 0.05, and the shear component is about 0.20; whereas the respective values for the second strain are 0 and 0.16. Because of the large stresses that must be associated with the normal component of strain during the first strain (the resisting stresses are compressional), it is likely that hydrostatic components of stress would affect the course of the transformation. This prediction, which was pointed out by S. A. Kulin, was recently confirmed by him at M.I.T.

**Evaluation of Theories Describing the Formation of Martensitic Plates:** There are at least three theoretical descriptions of the formation of a martensitic plate. One can be described as an atom-by-atom diffusion growth under the influence of coherency.<sup>9, 10</sup> Another is the mechanism described by



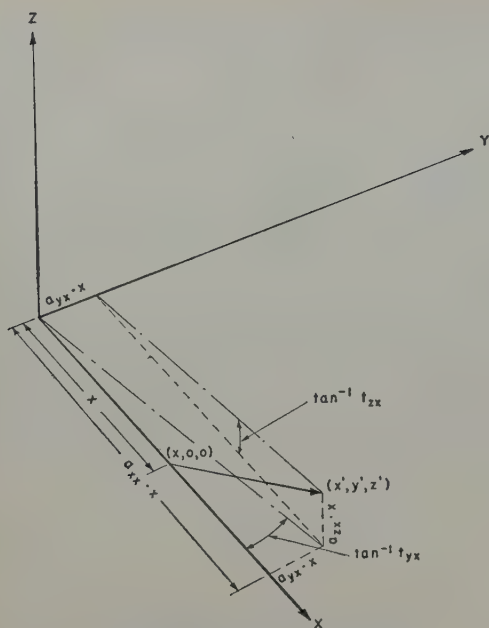


Fig. 13—Relationships between components of  $T$  matrix and coordinate-transformation matrix  $A$ .

Bowles as the growth by addition of one plane of atoms at a time. Still another is the wave-propagation method described in this paper.

The fact that the measured strain does not yield the martensite lattice, and the probable physical existence of the second strain heterogeneously distributed over the macroscopic plate, both testify against the likelihood of atom-by-atom movements. The requirement of succession in order of application of the two strains and the fact that the measured strain is a consistent invariant-plane strain also point up the improbability of atom-by-atom growth. Furthermore, the diffusion growth process does not seem to be a useful mechanism for the martensitic transformation from the standpoint of interpreting the crystallography involved.

With regard to the second mechanism, the  $\{259\}_A$  planes rotate during the second strain, and this means that a plate cannot grow by addition of one  $\{259\}_A$  plane at a time, with rotation of the  $\{259\}_A$  plane on the martensite side of the interface and no rotation of the  $\{259\}_A$  plane on the other side. Also, the requirement in this theory for a plate nucleus of almost final plate length and width lying along the  $\{259\}_A$  plane makes the Bowles plane addition mechanism highly improbable.

The remaining mechanism based on the propagation of the transformation strain as a wave has been shown to be a reasonable one in the text of this paper. Of the three mechanisms, it is the only one that yields consistent explanations for the known facts.

### Summary and Conclusions

1—All measured transformation strains for the austenite-martensite reaction are crystallographically equivalent in a given habit system. This suggests that, in general, only one reaction path operates in a given habit system.

2—The measured strain does not produce the martensite lattice from the austenite lattice. However, a sequence of two strains can generate the martensite in the correct orientation with respect to the austenite.

3—Each of these two strains can be described as

a homogeneous strain involving the motion of an invariant plane, i.e., a plane of no rotation and no distortion. The second strain is (close to) a simple shear, while the first strain is not. The second strain is homogeneous only over small regions compared to the volume of the martensitic plate.

4—The two strains obtained are consistent with the Bowles double-strain analysis for the  $\{259\}_A$  as well as the  $\{225\}_A$  habit systems. The measured strain is one of the Bowles strains and is therefore a homogeneous, invariant-plane type of strain.

5—From the latter result and the matrix analysis, it is deduced that there is a sequence to the operation of the strains in  $\{259\}_A$  systems as follows:

|                          | First Strain<br>(Measured Strain) | Second Strain |
|--------------------------|-----------------------------------|---------------|
| Invariant plane          | $(259)_A$ within $2^\circ$        | $(235)_M$     |
| Direction of atom motion | $[156]_A$ within $2^\circ$        | $[111]_M$     |

6—The observed habit plane lies parallel to, and is determined by, the invariant plane of the first strain. The parallelism helps minimize the strain energy developed during the formation of the plate.

7—The Bowles invariant-type, double-strain analysis does not yield a unique prediction for the habit plane. However, this prediction becomes possible when the following additional principle is introduced. The second direction of atom motion lies along the only remaining close-packed direction in the unrotated close-packed plane after the first strain.

8—The conclusion is reached that the Kurdjumow-Sachs orientations correspond to  $\{225\}_A$  habit planes and the Greninger-Troiano orientations correspond to  $\{259\}_A$  habit planes.

9—Metallographic evidence is shown for the existence of a macroscopically heterogeneous strain, corresponding to the predicted second strain.

10—The order of magnitude of the measured strain is quite large, about 0.1.

11—The martensitic transformation in  $\{259\}_A$  habit systems should be about twice as cooperative as in  $\{225\}_A$  habit systems. This follows from the fact that there are twice as many habit permutations in the former compared to the latter. Also there is a correspondingly greater tendency for groups of martensitic plates to move the intervening austenite in the same direction, thus minimizing the strain energy generated and allowing the plates formed to grow thicker than isolated plates.

12—The reaction-path description of the martensitic transformation is found to be more useful and more likely than the other proposed mechanisms.

### Acknowledgments

The authors gratefully acknowledge the support of the Office of Naval Research in this program. The micrographs of Fig. 10 were kindly supplied by W. J. Harris, Jr. of the Naval Research Laboratory.

### Appendix I

#### Derivation of Relations between Measured $T$ Matrices and the Coordinate-Transformation Matrices

Suppose the coordinate-transformation matrix representing a certain strain is  $A$  where:

$$A = \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \quad [A-1]$$

A point  $(x, 0, 0)$  is then transformed by this matrix to:

$$(x', y', z') = (a_{xx} x, a_{yx} x, a_{zx} x) \quad [A-2]$$



Now  $t_{yz}$  is the tangent of the angle between the  $X$  direction and the final position of this line projected onto the  $Z$  plane (Figs. 1 and 13). As shown in Fig. 13,  $t_{yz}$  is related to the components of  $A$  by the following equation:

$$t_{yz} = \frac{a_{yx} \cdot X}{a_{zx} \cdot X} = \frac{a_{yx}}{a_{zx}} \quad [A-3]$$

$$t_{zx} = \frac{a_{zx} \cdot X}{a_{xx} \cdot X} = \frac{a_{zx}}{a_{xx}} \quad [A-4]$$

By similarly investigating the transformation of points in the  $Y$  and  $Z$  axes, the following relations are obtained:

$$t_{xy} = \frac{a_{xy}}{a_{yy}} \quad t_{xz} = \frac{a_{xz}}{a_{zz}} \quad [A-5]$$

$$t_{zy} = \frac{a_{zy}}{a_{yy}} \quad t_{yx} = \frac{a_{yx}}{a_{xx}} \quad [A-6]$$

The diagonal components  $t_{xx}$ ,  $t_{yy}$ ,  $t_{zz}$  need not be discussed here because they are unnecessary to the analysis and have not been measured. They represent extensions or contractions and are difficult to determine.

**Calculation of Equivalence of  $T$  Matrices:** Because the  $Z$  axis is the  $[111]_A$  direction (Fig. 1), there exists a three-fold symmetry about this axis. Thus, a counter-clockwise and clockwise rotation by  $120^\circ$  should yield crystallographically equivalent matrices; that is, transformations in which the reaction path during the transformation is exactly the same.

In order to ascertain which of the  $T$  matrices are equivalent, values of the diagonal components are required. Such values have been approximated in Appendix III. It was found that  $T'_a$ ,  $T'_c$ , and  $T'_e$  are related to one another by  $120^\circ$  rotations about  $[111]_A$ , and similarly for  $T'_b$ ,  $T'_d$ ,  $T'_f$ . Furthermore, in investigating the relation between the single-prime matrices and the double-prime matrices, it was also found that any one single-prime matrix has a mirror symmetry with one of the double-prime matrices across a  $\{110\}_A$  plane. Thus, it may be concluded that all the matrices are crystallographically equivalent in that they represent the same crystallographic reaction path.

The best choice found for  $T'_a$  is:

$$\begin{pmatrix} 1.013 & 0.011 & \overline{0.03} \\ 0.10 & 1.079 & \overline{0.22} \\ 0 & 0 & 1 \end{pmatrix}$$

and for  $T'_b$  is:

$$\begin{pmatrix} 0.99 & 0.11 & \overline{0.16} \\ \overline{0.01} & 1.09 & \overline{0.14} \\ 0 & 0 & 1 \end{pmatrix}$$

## Appendix II

### Can a Body-Centered Cubic Structure be Obtained From the Measured Strain?

Inasmuch as the nondiagonal components of the  $T$  matrices (the only measured components) will yield the final positions of the axes (Fig. 1), the final angles between axes to determine whether the measured strain generates a body-centered cubic structure can be investigated.

From all the X-ray determinations of lattice orientations, it is found that at least one  $\{110\}_M$  plane is parallel to a  $\{111\}_A$  plane.\* From the work of Gren-

\* Actually, it can be deduced from the work of Greninger and Troiano that all close-packed planes in the austenite become  $\{110\}$  planes in the martensite.

\*\* It should be remembered in considering Fig. 14 that the original positions of the atoms are close-packed. This consideration places a limit on the possible choices of transformed directions corresponding to the original close-packed directions.

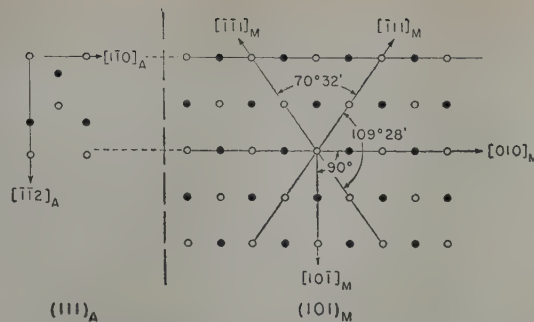


Fig. 14—Arrangements of atoms in  $(111)_A$  and  $(101)_M$  showing the three possible sets of choices of martensite directions derivable from  $[110]_A$  and  $[112]_A$ .

Note: Closed circles lie in next plane above plane of open circles.

inger and Troiano (Fig. 6 of ref. 4), it is also known that the pole of this  $\{111\}_A$  plane lies in the same octant on the stereographic projection as the pole of the habit plane. Using this knowledge and the fact that all the habit planes corresponding to the  $T$  matrices lie in the same octant as  $(111)_A$ , it may be concluded that  $(111)_A$  becomes  $(101)_M$ . This means that the final position of the  $(111)_A$  plane after the transformation is unrotated with respect to its initial orientation. In addition, the fact that  $t_{xx} = t_{yy} = 0$  shows that the  $(111)_A$  plane does not rotate during the first strain. Also, the fact that  $t_{xy} \neq 0$  and  $t_{yz} \neq 0$ , shows that the  $(111)_A$  is not the invariant plane of the first strain. Hence, the  $(111)_A$  must lie in the zone of the direction of motion of the invariant plane.

The next step is the determination of the angles between the deformed positions of the  $X$  and  $Y$  axes. According to the convention of sign, the final angle between the  $X$  and  $Y$  axes, providing  $t_{xx} = t_{yy} = 0$ , is:

$$90^\circ - \tan^{-1} t_{yz} - \tan^{-1} t_{xy}$$

Inasmuch as  $t_{xx} = t_{yy} = 0$  for all the  $T$  matrices, this angle can be calculated and for  $T'_a$  is:

$$90^\circ - \tan^{-1} 0.01 - \tan^{-1} 0.10 = 83^\circ 40'$$

There exists an experimental uncertainty in both  $t_{xy}$  and  $t_{yz}$ . Taking the extremes, the uncertainty in this transformed angle is about  $\pm 1^\circ 30'$ .

Reference to Fig. 14 shows that the most probable choices of angles for this "deformed" angle in the final body-centered cubic martensite are  $90^\circ$ ,  $70^\circ 32'$ , and  $109^\circ 28'$ .\*\* All these choices are out of the experimental range found ( $83^\circ 40' \pm 1^\circ 30'$ ) and hence it may be deduced that the structure corresponding to the measured strain is not martensite. Further calculations assuming the strain to be characterized by an invariant plane (Appendix III) shows unequivocally that the structure corresponding to the measured strain is not martensite.

## Appendix III

### Calculation of Invariant Planes and Directions of Atom Motion Corresponding to Measured $T$ Matrices

Now that the coordinate-transformation matrix has been related to the measured  $T$  matrix,  $A$  can be derived on the basis that in the transformation there exists at least one plane of no distortion and no rotation.

Let a set of coordinates be chosen in the following manner: The  $Z_1$  axis is taken perpendicular to this plane of no distortion and no rotation. Then consider the most general motion of this invariant plane; that is, motion in a direction not contained in the plane. The  $X_1$  axis is chosen to lie in the invariant plane and in the plane defined by the direction of motion and the  $Z_1$  axis. The  $Y_1$  axis defined by a right-handed set (as in Fig. 13) then lies in the invariant plane. Relative to these coordinates the most general coordinate transformation matrix which leaves the  $X_1Y_1$  plane undistorted and unrotated is:

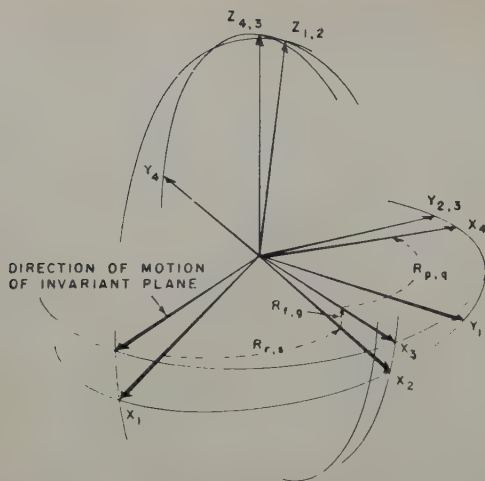


Fig. 15—Positions of coordinate axes and rotations used to illustrate matrix analysis for determining the experimental first invariant plane and direction of atom motion.

$$A_1 = \begin{pmatrix} 1 & 0 & m \\ 0 & 1 & 0 \\ 0 & 0 & 1+n \end{pmatrix} \quad [A-7]$$

To show that this matrix has the properties claimed for it, operate with this matrix on any  $X_1Y_1$  plane, i.e.  $z = c$ :

$$\begin{pmatrix} x_1' \\ y_1' \\ z_1' \end{pmatrix} = \begin{pmatrix} 1 & 0 & m \\ 0 & 1 & 0 \\ 0 & 0 & 1+n \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ c \end{pmatrix} \quad [A-8]$$

or:

$$\begin{aligned} x_1' &= x_1 + cm \\ y_1' &= y_1 \\ z_1' &= c(1+n) \end{aligned}$$

Thus, the plane at  $z_1 = c$  is carried into a plane parallel to itself at  $z_1 = c(1+n)$ . Further, it can be proved that distances and angles in the plane are preserved. Hence, the  $X_1Y_1$  plane is an invariant plane.

Now, however, the matrix  $A_1$  must be converted into an equivalent matrix in the coordinate system used in the measurements because the  $X_1Y_1Z_1$  axes are arbitrary in these considerations. This calculation can be performed either step-wise or in one operation. Inasmuch as it is easier to visualize the resulting quantities from the step-wise calculation, the discussion will be from this point of view.

The equivalent matrix  $A_4$  in the coordinate system used for the measurements can be derived from  $A_1$  by a series of three rotations as described in Fig. 15, namely,  $R_{r,s}$ ;  $R_{f,g}$  and  $R_{p,q}$ . The subscripts in the above are respectively the cosine and sine between the axes shown for the respective rotations. Using matrix algebra, the equivalent matrix is obtained as follows:

$$\begin{aligned} A_4 &= R_{p,q}^{-1} R_{f,g}^{-1} R_{r,s}^{-1} A_1 R_{r,s} R_{f,g} R_{p,q} \\ &= \begin{pmatrix} 1 + p^2n + pqgms & -pqn - q^2gms & pmr - qfms \\ -pqn + p^2gms & 1 + q^2n - pqgms & -qmr - pfms \\ 0 & 0 & 1 \end{pmatrix} \\ &= \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \end{aligned} \quad [A-9]$$

As shown by eq A-9 there are certain relations between the derived experimental quantities  $a_{ij}$  and the components of  $A_4$ . These relations make the determination of the invariant plane possible and are:

$$-\frac{p}{q} = \frac{a_{yx} a_{xz}}{a_{xy} a_{yz}} \quad [A-10]$$

$$\frac{g}{f} = \frac{a_{xy} - a_{yz}}{qa_{xz} + pa_{yz}} \quad [A-11]$$

$$n = -\left(\frac{p}{q} a_{xy} + \frac{q}{p} a_{yz}\right) \quad [A-12]$$

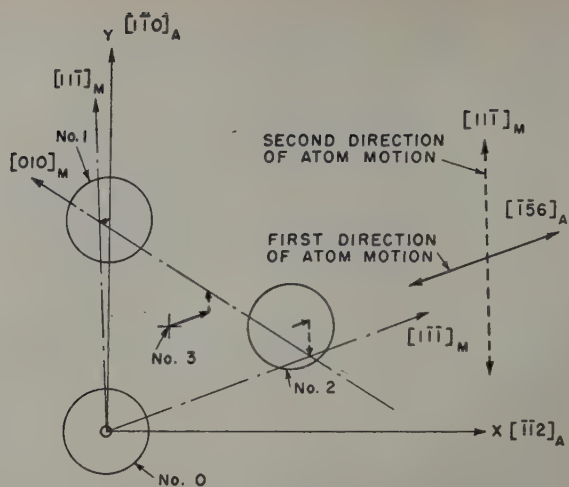


Fig. 16—Motion of atoms of primitive tetrahedral cell of austenite during transformation to martensite.

Motions lie in plane of paper which is  $(111)_A \parallel (101)_M$ . Atom No. 3 lies in plane above the plane containing atoms No. 0, 1, and 2.

$$\frac{r}{s} = -\frac{fn}{a_{yx} - a_{xy}} \quad [A-13]$$

and

$$m = -\frac{fn}{gr} \quad [A-14]$$

Because the diagonal components  $t_{xx}$ ,  $t_{yy}$ ,  $t_{zz}$  have not been measured, it is necessary to use an approximation method to obtain the values of the components of  $A_4$  as follows:

1—Assume  $a_{ij} = t_{ij}$  and calculate values of  $p$ ,  $q$ ,  $f$ ,  $g$ ; ( $gms$ ) and  $n$  using eqs A-10 to A-14.

2—With these tentative values of cosines and sines, calculate first approximations of the diagonal components  $a_{xx}$ ,  $a_{yy}$ ,  $a_{zz}$  using eq A-9.

3—Using these values of the diagonal components, recalculate the second approximations of the nondiagonal components and repeat steps 1 to 3 until the computed values of  $a_{ij}$  do not change measurably with further approximations.

It was found that the second approximations of  $a_{ij}$  were sufficient since rapid convergence existed.

The second-approximation solutions corresponding to  $T_a'$  and  $T_b''$  are:

|         | $p/q$  | $g/f$       | $r/s$       |
|---------|--------|-------------|-------------|
| $T_a'$  | -1.29  | $\pm 0.581$ | $\pm 0.878$ |
| $T_b''$ | +0.100 | $\pm 0.685$ | $\pm 0.61$  |

In using these values, care must be taken to be consistent in sign for any particular choice of sign of  $p$  and  $f$ . Otherwise the solutions are liable to result in rotations in the wrong directions.

On carrying through the calculated rotations for the solutions to  $T_a'$ ,  $T_b''$ , and their crystallographic equivalents, the results shown in Figs. 3 and 4 are obtained.

## Appendix IV

### Calculation of Elements of Second Strain

The elements of the second strain can be determined by the following procedure:

1—Calculate the positions of the atoms defining the primitive tetrahedral cell in austenite after the first strain relative to the austenite lattice.

2—Pick the orientation of the martensite lattice relative to the austenite and transform the positions found in 1 to be relative to the martensite axes.

3—Select the nearest positions of these atoms that would correspond to the martensite structure.

4—Calculate the coordinate transformation matrix required to transform the atoms from the positions found in 2 to their respective positions chosen in 3.



5—Analyze this matrix according to the method outlined in Appendix III.

Carrying through this procedure using  $T_c'$  to determine the positions of the atoms after the first strain, the following results are obtained (Fig. 16):

| Atom | After First Strain                  |                                      |                                     |
|------|-------------------------------------|--------------------------------------|-------------------------------------|
|      | Position Relative to Austenite Axes | Position Relative to Martensite Axes | Nearest Atom Position in Martensite |
| (1)  | (0.113, 2.47, 0)                    | (0, 2.475, 0)                        | (0, 2.477, 0)                       |
| (2)  | (2.36, 1.33, 0)                     | (2.42, 1.22, 0)                      | (2.34, 0.83, 0)                     |
| (3)  | (1.17, 1.44, 2.06)                  | (1.24, 1.39, 2.06)                   | (1.17, 1.65, 2.02)                  |

The matrix relating the atom positions after the first strain to those in the final martensite is found to be:

$$B = \begin{pmatrix} 0.96 & 0 & 0.0113 \\ 0.163 & 1 & 0.224 \\ 0 & 0 & 0.98 \end{pmatrix}^{***}$$

Solving this  $B$  matrix according to the method outlined in Appendix III yields the results given in Fig. 5 for the elements of the second invariant-plane strain. The  $B$  matrix corresponding to the second strain is also used in Appendix V to test for the sequence of strains.

## Appendix V

### Non-Commutability of First and Second Strains

If the first and second strains are commutable, i.e., interchangeable in their sequence, then  $AB = BA$ . Checking with the  $T_c'$  case as an example:

$$AB = \begin{pmatrix} 1.109 & 0.045 & 0.205 \\ 0.045 & 0.980 & 0.084 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0.96 & 0 & 0.0113 \\ 0.163 & 1 & 0.224 \\ 0 & 0 & 0.98 \end{pmatrix}$$

$$AB = \begin{pmatrix} 1.070 & 0.045 & 0.199 \\ 0.117 & 0.980 & 0.138 \\ 0 & 0 & 0.98 \end{pmatrix} \quad [A-15]$$

\*\*\* The (zz) component has been taken as equal to 1 in finding the plane of invariance for this matrix. This corresponds to the approximation used by Bowles, namely that of neglecting the change in atom radius due to the change in coordination number.

$$BA = \begin{pmatrix} 1.063 & 0.043 & 0.186 \\ 0.136 & 0.987 & 0.173 \\ 0 & 0 & 0.98 \end{pmatrix} \quad [A-16]$$

Thus  $AB \neq BA$ , and the matrix multiplication is not commutative.

Because  $A$  and  $B$  are the invariant-plane solutions for the first and second strains, and the order of application of  $A$  followed by  $B$  (see Appendix IV) yields the correct final orientation, then this sequence must be followed physically.

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## Technical Note

### Metallographic Techniques for Austenite Grain Size of Steels in the As-Cast State

by Edward A. Loria

A SERIES of papers on the study of austenite grain size in cast steels has been published recently.<sup>1-5</sup> These studies show that in the as-cast state, the austenite grains are quite large, for they form as the steel freezes at a very high temperature, but a simple reheating above the critical range produces a new

set of austenite grains which, in many instances, is finer than ASTM grain size No. 8. Furthermore, there is no apparent relationship between as-cast austenite grain size and subsequent grain size produced by heat treatment.

The as-cast austenite grain size can be determined easily in plain carbon and low alloy steels which produce a continuous grain boundary ferrite envelope in the as-cast structure. In the case of cast steels whose alloy content produces greater hardenability and suppresses the proeutectoid ferrite transforma-

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TN 88E. Manuscript, July 13, 1951.



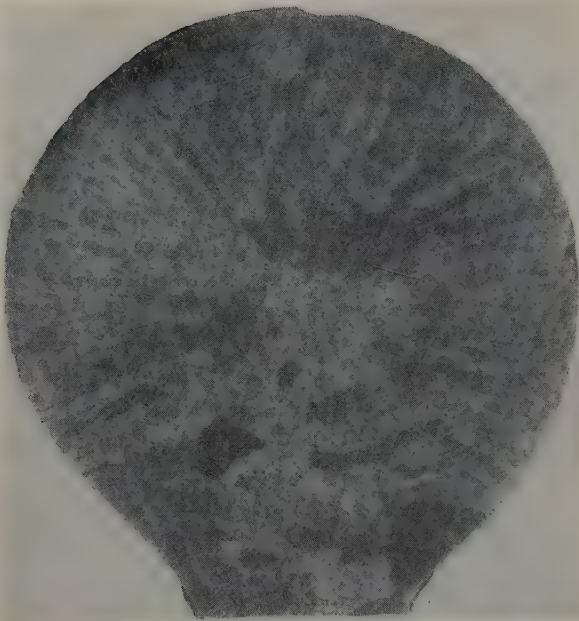


Fig. 1a—As-cast macrostructure of alloy cast steel containing 0.25 pct C, 1.05 pct Mn, 0.65 pct Ni, 0.61 pct Cr, and 0.22 pct Mo. Modified nitrosulphuric etch. X2. Area reduced approximately 20 pct for reproduction.

tion, there is no such indicator of the location of the original grain boundaries. Hence it becomes necessary to employ special etching reagents in order to bring out the structure. Perhaps some value for as-cast grain size determinations can be seen if consideration is given to the mechanism of diffusion and its relation to homogenization of structural components during heat treatment. Normally structural equilibrium is more rapidly attained with the smaller grain so that time of heat treatment required for homogenizing cast steels should normally decrease with decrease in austenitic grain size.

In a previous paper<sup>4</sup> the initial results on the use of a modified nitrosulphuric reagent in revealing the as-cast structure and grain size in a few cast alloy steels, which did not show ferrite outlining of the original grain boundaries, were shown. Such work has been continued in an effort to learn the quantitative effects of smaller initial grain size on homogenization of alloy cast steel. For this purpose the polished cross-sections of hardenability test bar castings have been subjected to the action of the modified nitrosulphuric reagent. Fig. 1a shows the excellent grain contrast that is produced across the 1½ in. diam bar of a popular grade of alloy cast steel. Such results can be obtained with this reagent when it consists of 20 ml concentrated nitric acid, 10 ml concentrated sulphuric acid, and 20 ml distilled water. The etching procedure was described previously.<sup>4</sup>

In steels exhibiting temper brittleness, it has been found that the addition of the wetting agent, Zephiran chloride, to a modified picral etch reveals a precipitate not shown by other etching reagents.<sup>5</sup> The excellent delineation of the grain outlines occurring in embrittled steel upon etching with the Zephiran reagent, particularly when the specimen is lightly repolished after etching, indicates that this agent would certainly assist in the search for the interfaces of as-cast grains. Therefore, 1 pct Zephiran chloride has been added to 4 pct nital and has increased the sensitivity of the latter and the speed of etching. Since the as-cast grains are quite large,

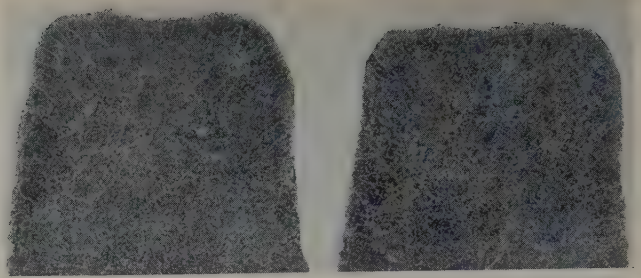


Fig. 1b—As-cast macrostructure of alloy cast steel containing 0.31 pct C, 1.44 pct Mn, 0.26 pct Mo. 6 pct nital-1 pct Zephiran chloride etch. X1.7. Area reduced approximately 20 pct for reproduction.

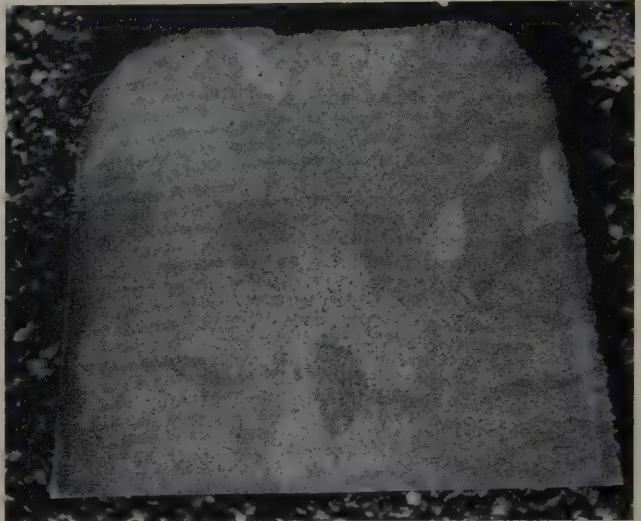


Fig. 1c—As-cast macrostructure of alloy cast steel containing 0.31 pct C, 1.44 pct Mn, 0.26 pct Mo. Modified nitrosulphuric etch. X2. Area reduced approximately 50 pct for reproduction.

a macroetch is really needed, and hence the best results have been obtained employing 1 pct Zephiran chloride in 6 pct nital. An example of the way this grain boundary etchant reveals the as-cast structure in conventional 1½x1¼ in. tensile test coupons of alloy cast steel is given in Fig. 1b. Each cross-section was immersed in the reagent until the grain boundaries became apparent visually. A comparison can be made with a similar sized coupon of the same alloy cast steel etched with the modified nitrosulphuric reagent and shown as Fig. 1c. Thus it can be seen that the modified nitrosulphuric reagent as a grain contrast etchant and the 6 pct nital-1 pct Zephiran chloride reagent as a grain boundary delineator are welcome additions to the tools available for the metallography of cast steels.

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# Low Sulphur Steel from High Sulphur Raw Materials and Fuel

by F. L. Robertson, C. H. Bacon, and J. W. Till

A description is given of the development of a process for making low sulphur steel on furnaces fired with 2½ pct sulphur oil. Slag and metal are analyzed at melt. Slag weight is estimated. A simple method for calculating necessary lime additions for making 0.025 and 0.035 pct sulphur steel is given.

DURING the last 15 years John Summers & Sons have been confronted increasingly by the problem of producing a low sulphur steel from high sulphur materials. The principles adopted, the processes used, the data collected on a furnace specially set aside to study this problem, and speculation on future developments are dealt with in this paper.

This study is limited to two melting shops which make sheet steel only, of the following analysis: C, 0.06 pct; Mn, 0.33; S, 0.04, 0.035, 0.03, and 0.025; and P, 0.02 and 0.015. All the processes described have reference to the manufacturing of this steel and are not necessarily applicable, without modification, to other steels. The raw materials used are given in Table I.

## Development of Process

About 1934, Schenck's work on phosphorus was applied to frame quantitative rules for the removal of phosphorus, with great success. We could however, neither in our own work nor in the voluminous literature, find any assistance to frame quantitative furnace rules to remove sulphur. Perhaps, we should have persevered with Schenck's outstanding chapter on sulphur in *The Physical Chemistry of Steelmaking*, but we missed the importance of one

sentence on p. 478. "Evidently this ratio  $\frac{(\sum S)}{[S]}$  is

the important quantity to be considered from the point of view of chemical reaction; it is clear that the sulphur content of the steel alone, as frequently given in the literature cannot suffice for judging the success of the reaction unless special details are given regarding the sulphur charge and the amount of slag."<sup>1</sup> We were not however very successful in getting values for Schenck's "η" that agreed with

$\frac{(\sum S)}{[S]}$  arrived at by our direct analysis.

In addition to Schenck's work much attention was given to V value. The formula selected for V was:

$$V = \frac{(\sum \text{CaO}) - 1.57 (\sum \text{P}_2\text{O}_5)}{(\sum \text{SiO}_2)}$$

After plotting many charges a curve was obtained, based upon the relationship between the percentage

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sulphur in the finished steel and V value, Fig. 1. For a long time this was used as standard with about a 60 to 70 pct success on producer-gas fired furnaces, if all uprising scrap was used and no bought scrap used. An inspection of this curve shows clearly that it is not a quantitative manufacturing process, and that it was not sure enough to go to the trouble and expense of doing stage analysis for  $\text{P}_2\text{O}_5$ ,

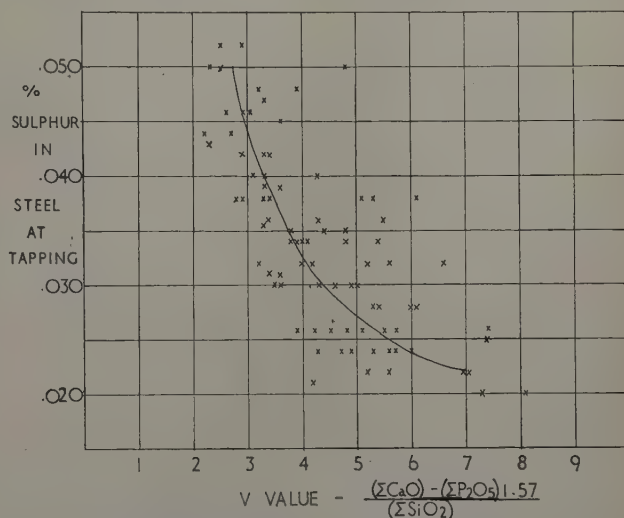


Fig. 1—Relationship between percentage of sulphur in steel and V value for producer-gas fired furnaces. (Coal 1 pct S.)

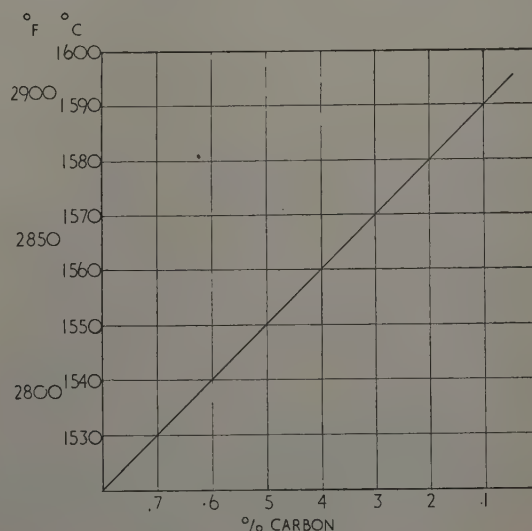


Fig. 2—Carbon/temperature curve.





CaO, and SiO<sub>2</sub>. At this time there was no problem in making as much 0.025 pct S steel as required, and other matters pressed.

In 1946, four oil (S = 2.5 pct) fired furnaces were introduced and it was found that conditions that had given 60 to 70 pct of 0.025 pct S charges on producer gas firing gave none on oil firing. Generally throughout the works, this was ascribed to the sulphur in the oil but, even yet, this is not proven for certain until more quantitative work is done to insure that the slag weights are equal in both cases. The works position was, however, so serious that the whole question of sulphur passage between the slag and steel was studied anew.

By this time Grant and Chipman's paper had appeared.<sup>2</sup> With this, and with Schenck's older work as a basis, work was started with a view to evolving a process for making steel of any specified sulphur content from the materials available.

With the combined assistance from many departments and Trade Union organization in the Works, a scheme was set up to work one furnace under special supervision and controlled conditions.

*Experimental Furnace Trials:* The furnace was fully instrumented and was given priority in operation. The object was to reduce the variables to a minimum, so that the relation between furnace practice and rate of output could be studied. This presented an opportunity to study sulphur in a way that had not been possible before. A full report of the furnace conditions and their relation to output is given in a paper by Robertson and Thring.<sup>3</sup> A short description of the conditions of the trial, insofar as they influence the investigation on sulphur, will be presented here.

Three roof pyrometers are fitted and the oil flow is controlled automatically from them. The control system is arranged to operate so that, as soon as one of the three pyrometers reaches the set maximum temperature, the oil flow is reduced. A maximum fuel flow controller is incorporated to operate before the maximum roof temperature is reached.

The furnace is charged with 58 tons of steel scrap and about 31 tons of cold machine-cast pig iron. When possible, the scrap used for these trials was all uprising scrap, consisting of slab crops and sheet clippings, to enable an estimate of the analysis to be made.

The actual weight of pig iron needed to give a carbon of 0.3 to 0.5 pct, when clear melted, is calculated by means of the oxygen equivalent. The oxygen equivalent per ton of iron is the weight of oxygen required to oxidize the C, P, Mn, and Si in one ton of iron to CO, P<sub>2</sub>O<sub>5</sub>, MnO, and SiO<sub>2</sub>. The figure for the total oxygen equivalent is found by experience on the furnace and this figure, divided by the oxygen equivalent per ton, gives the weight of pig iron required.

A standard charging sequence was introduced and processing during refining was controlled. Fig. 2 shows the carbon temperature curve adopted. Feeding of lime and ore was not permitted until the steel temperature, obtained by an immersion pyrometer, reached the figure on the curve corresponding to the carbon in the steel. The time at which this occurs is referred to as "junction," instead of the more commonly used "melt out." Junction is defined in the measurable terms of carbon and temperature and therefore is considered to have more value in control work than melt out, which is not capable of precise definition.

Table I. Analysis of Raw Materials, Percent

| Material              | C       | Si      | Mn       | S         | P        |
|-----------------------|---------|---------|----------|-----------|----------|
| 33 pct cold pig       | 3.5-3.8 | 0.4-1.2 | 0.75-1.5 | 0.03-0.07 | 0.75-1.5 |
| 33 pct uprising scrap | 0.06    |         | 0.3      | 0.04      | 0.02     |
| 33 pct bought scrap   | 0.2     |         | 0.5      | 0.06      | 0.06     |
| Burnt lime            |         |         |          | 0.1-0.2   |          |
| Spar                  |         |         |          | 0.6-0.8   |          |
| Oil                   |         |         |          | 2.3-2.7   |          |
| Coal                  |         |         |          | 0.9-1.4   |          |

Fig. 3 is a copy of one of the master charts. The individual furnace charts are copied on to this chart, and the following data is shown: charging sequence, roof temperature, oil flow, steam flow, air flow, furnace pressure, CO<sub>2</sub> and O<sub>2</sub> in waste gas, steel temperature rise, and carbon, sulphur and manganese drop.

The ingoing materials in the form of pig iron, lime, spar and ore are analyzed. Full analyses are also carried out on the metal and slag at junction and tapping. The calculation sheet, Fig. 4, is our approach to the study of the behavior of the carbon, silicon, phosphorus, sulphur, and oxidation during the course of the charge and their distribution between the metal, slag, and furnace atmosphere. The top line in each case represents the percentage of the element present. The second line shows the weight of the element (all weights shown are in tons, except sulphur, which is in pounds. References to tons in this paper have been converted to short tons). The third line gives the weight of oxygen that will combine with the element, and the fourth line gives the weight of the oxide formed. The balances for the oxidation, sulphur, and silicon are shown on the right.

In the case of the sulphur balance, the weight of sulphur introduced through the pig iron and scrap is shown under "Metals," and from the lime and spar under "Nonmetals." The difference between the weight of sulphur in the system at junction and the weight of sulphur in the charge gives the weight of sulphur absorbed from, or lost to, the furnace atmosphere. Analysis of the tapping samples enables a second balance to be made showing the pick up or loss between junction and tapping, after making allowance for any sulphur introduced with the feeds.

This information is set out in a rather different form in Fig. 5. This flowsheet proved to be the most helpful approach to the study of the behavior of sulphur. The important points that emerged from the careful study of a large number of sulphur flowsheets were:

- 1—That the  $\frac{(S)}{[S]}$  value at junction varied greatly.
- 2—That the  $\frac{(S)}{[S]}$  value at tapping varied considerably, but that the bulk of the results were in excess of 6. Fig. 6 shows the range of  $\frac{(S)}{[S]}$  at tapping for 250 charges.
- 3—That the pickup of sulphur from the furnace atmosphere varied within wide limits, but that the average figures could be taken as 30 lb between start charge and junction and nil between junction and tapping.

Figs. 7 and 8 are histograms showing the spread

Fig. 4—Calculation Chart, Cast L204

(Continued→)

| Time Operation<br>A.M. | Time<br>from<br>S.C. | Materials Charged and Fed   |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|------------------------|----------------------|-----------------------------|-------|--------|-------|-------|------|------|--------|-------|------|------|------------------|--------|-----|-----------------|------|
|                        |                      | Pig Iron                    |       |        |       |       |      |      | Scrap  |       |      |      | Lime             |        |     |                 |      |
|                        |                      | C                           | Si    | S      | P     | Mn    | Fe   | Wt   | S      | Mn    | Fe   | Wt   | SiO <sub>2</sub> | S      | CaO | CO <sub>2</sub> | Wt   |
| 9:20 Start charging    |                      |                             |       |        |       |       |      |      | 0.038  | 0.37  | 99.6 |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      | 0.0238 | 0.232 | 62.5 | 62.7 |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      | 47.7*  | 0.067 |      |      |                  |        |     |                 |      |
|                        |                      | 4.02                        | 0.94  | 0.026  | 0.92  | 1.35  | 93.7 |      |        |       |      |      | 0.60             | 0.12   |     |                 |      |
|                        |                      | 1.18                        | 0.276 | 0.0076 | 0.271 | 0.397 | 27.6 | 29.4 |        |       |      |      | 0.028            | 0.0056 |     |                 | 4.7  |
| 2:20 Finish charging   | 5.0                  | 1.57                        | 0.315 | 15.2*  | 0.348 | 0.115 |      |      |        |       |      |      |                  | 11.2*  |     |                 |      |
|                        |                      | 0.591                       |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 4:35 Spar              |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 5:25                   |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 6:00                   |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 6:25                   |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 6:50                   |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 6:50 Temperature       |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 7:20 Sampled           | 10.0                 | Carbon-temperature junction |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 7:25 Ore               |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 7:50 Temperature       |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 7:55 Lime and ore      |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 | 0.67 |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 8:20 Temperature       |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 8:25 Lime              |                      |                             |       |        |       |       |      |      |        |       |      |      | 0.008            | 0.0016 |     |                 | 0.67 |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  | 3.1*   |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 8:45 Temperature       |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| 8:55 Tapped            | 11.58                |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
|                        |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |
| Pit sample             |                      |                             |       |        |       |       |      |      |        |       |      |      |                  |        |     |                 |      |

\* All weights in tons (2000 lb per ton) except sulphur, in lb.

Calculation Chart

(Continued→)

| Time Operation<br>A.M. | Time<br>from<br>S.C. | Steel |        |       |       |      |      | Oxidation              |             |               |              |           |                        |             |               |              |           |
|------------------------|----------------------|-------|--------|-------|-------|------|------|------------------------|-------------|---------------|--------------|-----------|------------------------|-------------|---------------|--------------|-----------|
|                        |                      |       |        |       |       |      |      | Cumulative             |             |               |              |           | From Junction          |             |               |              |           |
|                        |                      | C     | S      | P     | Mn    | Fe   | Wt   | O <sub>2</sub><br>Abs* | From<br>Ore | From<br>Flame | Pct<br>Flame | Per<br>Hr | O <sub>2</sub><br>Abs* | From<br>Ore | From<br>Flame | Pct<br>Flame | Per<br>Hr |
| 9:20 Start charging    |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 2:20 Finish charging   | 5.0                  |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 4:35 Spar              |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 5:25                   |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 6:00                   |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 6:25                   |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 6:50                   |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 6:50 Temperature       |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 7:20 Sampled           | 10.0                 |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
|                        |                      | 0.31  | 0.038  | 0.017 | 0.165 | 99.6 |      | 5.74                   | Nil         | 5.74          | 100          | 0.574     |                        |             |               |              |           |
|                        |                      | 0.26  | 0.0319 | 0.014 | 0.138 | 83.5 | 83.9 |                        |             |               |              |           |                        |             |               |              |           |
|                        |                      | 0.335 | 63.8*  | 0.019 | 0.042 |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 7:25 Ore               |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 7:50 Temperature       |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 7:55 Lime and ore      |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 8:20 Temperature       |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 8:25 Lime              |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 8:45 Temperature       |                      |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
| 8:55 Tapped            | 11.58                |       |        |       |       |      |      |                        |             |               |              |           |                        |             |               |              |           |
|                        |                      | 0.045 | 0.032  | 0.011 | 0.10  | 99.6 |      | 7.14                   | 0.100       | 7.04          | 98.5         | 0.608     | 1.4                    | 0.100       | 1.3           | 92.8         | 0.822     |
|                        |                      | 0.037 | 0.0261 | 0.009 | 0.082 | 81.4 | 81.6 |                        |             |               |              |           |                        |             |               |              |           |
|                        |                      | 0.049 | 52.2*  | 0.012 | 0.024 |      |      |                        |             |               |              |           |                        |             |               |              |           |
| Pit sample             |                      |       | 0.030  |       |       |      | 84.8 |                        |             |               |              |           |                        |             |               |              |           |

7.35 tons per hr  
50.6 lb per sq ft per hr



| Materials Charged<br>and Fed—Continued |        |                   |                  |       |  |                  |   |       |      | Slag                                   |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|----------------------------------------|--------|-------------------|------------------|-------|--|------------------|---|-------|------|----------------------------------------|------------------|-------|--------------------------------|--------------------------------|-------|---------------------|-------|-------------------------------|-------|------|----|--|
| Spar                                   |        |                   |                  |       |  | Swedish Ore      |   |       |      | Immer-<br>sion<br>Tempera-<br>ture, °F |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
| SiO <sub>2</sub>                       | S      | CaCO <sub>3</sub> | CaF <sub>2</sub> | Wt    |  | SiO <sub>2</sub> | P | Fe    | Wt   |                                        | SiO <sub>2</sub> | FeO   | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | MnO   | CaO                 | MgO   | P <sub>2</sub> O <sub>5</sub> | S     | "V"  | Wt |  |
| 16.9                                   | 0.30   |                   |                  |       |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
| 0.052                                  | 0.0009 |                   |                  | 0.308 |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        | 1.8*   |                   |                  |       |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      | 2809                                   | (Σ Fe) 19.3 pct  |       |                                |                                |       | Excess Base = 0.420 |       | (S)<br>= — 7.7<br>[S]         |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        | 6.2              | 20.4  | 4.8                            | 1.93                           | 7.8   | 48.8                | 3.84  | 5.44                          | 0.28  | 6.5  |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        | 0.597            | 1.96  | 0.462                          | 0.186                          | 0.751 | 4.7                 | 0.37  | 0.524                         | 0.027 | 9.6  |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        |                  | 0.438 | 0.14                           |                                |       |                     |       |                               | 54.0* |      |    |  |
|                                        |        |                   |                  |       |  | 5.9              |   | 59.0  |      | 2894                                   |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       | 0.22 |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  | 0.026            |   | 0.26  | 0.22 |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   | 0.100 |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      | 2903                                   |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      | 2885                                   | (Σ Fe) 23.7 pct  |       |                                |                                |       | Excess Base = 0.428 |       | (S)<br>= — 7.8<br>[S]         |       |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        | 4.8              | 23.3  | 8.0                            | 1.84                           | 6.2   | 46.2                | 4.53  | 4.45                          | 0.25  | 8.2  |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        | 0.86             | 4.17  | 1.48                           | 0.33                           | 1.11  | 8.3                 | 0.811 | 0.797                         | 0.044 | 17.9 |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        |                  | 0.927 | 0.432                          |                                |       |                     |       |                               | 89.6* |      |    |  |
|                                        |        |                   |                  |       |  |                  |   |       |      |                                        |                  |       |                                |                                |       |                     |       |                               |       |      |    |  |

7.35 tons per hr  
 50.6 lb per sq ft per hr

[illegible]

TRANSACTIONS AIME

for these values. Further study of the results gradually led to the conclusion that an understanding of the behavior of sulphur between the liquid phases could not be reached, unless the weight of the slag and the weight of the steel and the total weight of the sulphur in each were taken into account, besides the percentage of sulphur in the steel and the percentage of sulphur in the slag.

The Partition law cannot be used as a foundation for an extraction process, unless the weights of the two liquid phases, together with the total weight of the substance to be extracted, are taken into account, besides the ratio of the percentage concentrations of the substance in the two liquid phases.

This fundamental principle of the proper application of the Partition law, so well and so long understood in other industries, had escaped, not only ourselves, but other workers in the field. Except for one sentence in Schenck, to which reference has been made, no reference has been found in steel sulphur literature to the fact that consideration of percentages of sulphur in slag and steel is not enough without the weights of steel and slag, and weights of sulphur in each.

At this point we wish to give our apologies to Donald E. Babcock for not acknowledging his work in The American Iron and Steel Institute Proceedings of May 1949.<sup>4</sup> We would explain that our process was worked out and in operation on all furnaces in November 1948. We even venture to regret that Mr. Babcock, who clearly agrees with us, has been tempted to assume a constant slag weight in many of his examples.

**Sulphur Partition  $\frac{(S)}{[S]}$**  : Most of the literature concerning sulphur in steel is confined to the distribution of sulphur between steel and slag as measured by:

$$\frac{\text{Pct Sulphur in Slag}}{\text{Pct Sulphur in Steel}}$$

Numerous formulas have been evolved giving different degrees of effect upon this partition ratio to the lime, magnesia, manganese, iron oxide, silica, and alumina contents of the slag. Several of these formulas have been tested and compared with the partition figure obtained by direct analysis of steel and slag for sulphur. For our class of steel, closer agreement has been found with Grant and Chipman's Excess Base figures than with any other formula that has been tried.

Fig. 9 is a copy from Grant and Chipman's paper showing the relation between the calculated Excess

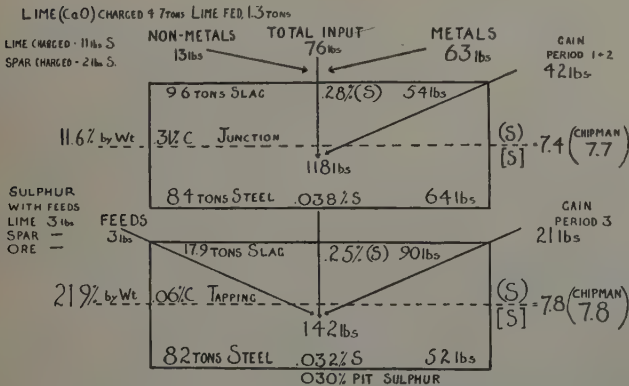


Fig. 5—Sulphur flowsheet, cast L204.

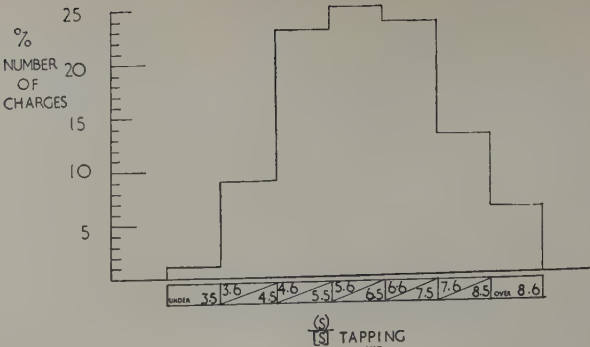


Fig. 6—  $\frac{(S)}{[S]}$  at tapping, 250 charges.

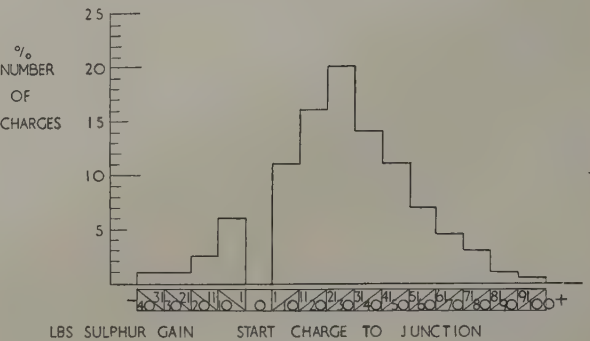


Fig. 7—Sulphur gain. Start charge to junction. 250 charges.

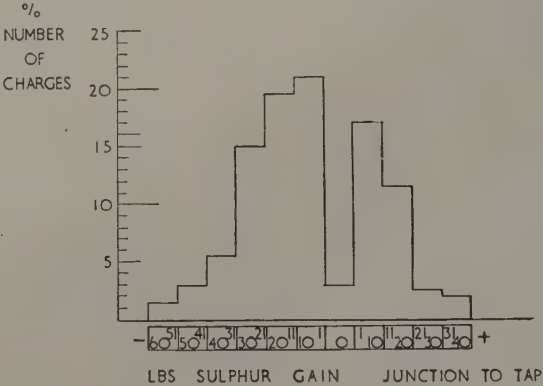


Fig. 8—Sulphur gain. Junction to tap. 250 charges.

Base figure and  $\frac{(S)}{[S]}$  by analysis for steel and slag samples from open hearth furnaces. Fig. 10 shows the results for 50 of our charges plotted on the same scale. It will be observed that our results show a very similar pattern to the former with a tendency for the higher  $\frac{(S)}{[S]}$  plots to be rather above the standard line.

It is obvious that the higher the  $\frac{(S)}{[S]}$  that can be obtained at tapping, the lower will be the slag weight that need be carried for a given sulphur burden and a given desired sulphur percentage in the steel. So, any formula that will give an insight into the factors that are conducive to a high  $\frac{(S)}{[S]}$  is valuable as a guide to the slag composition that will give the best possible desulphurization of the metal. For a process which is based upon the calcula-



tion of the feed lime required for individual charges, however, it has not been regarded as feasible to predict the  $\frac{(S)}{[S]}$  for each charge by any basicity measurement. Therefore our process has been based upon an expected  $\frac{(S)}{[S]}$  of 6.0 at tapping. Frequently figures are obtained that are considerably in excess of 6, but the process must necessarily be based upon a figure rather below the mean, for safety.

*Basis for a Process:* At this juncture it became apparent that the basis for a process must consist in increasing the slag weight, so that, at tapping, the percentage of sulphur in the slag is 6 times the percentage of sulphur desired in the metal, and that a means must be found to express this quantitatively in terms of lime additions. A calculation to determine the slag weight necessary for specified sulphur percentage in the steel, in terms of total weight of sulphur in the system and  $\frac{(S)}{[S]}$  follows.

- $W$  = Weight of steel, lb
- $w$  = Weight of slag, lb
- $P$  = Percentage of slag weight of steel weight
- $[S]$  = Percentage of sulphur in steel
- $(S)$  = Percentage of sulphur in slag
- $TS$  = Total weight, lb, of sulphur in steel and slag
- $L$  = Weight of sulphur in steel, lb
- $TS - L$  = Weight of sulphur in slag, lb
- $A = \frac{\text{Pct Sulphur in Slag}}{\text{Pct Sulphur in Steel}}$

$$\begin{aligned} \text{Then } A &= \frac{(S)}{[S]} = \frac{\frac{(TS-L) \times 100}{w}}{\frac{L \times 100}{W}} \\ &= \frac{TS-L}{L} \times \frac{W}{w} \\ &= \left( \frac{TS}{L} - 1 \right) \times \frac{W}{w} \\ &= \left( \frac{TS}{L} - 1 \right) \times \frac{100}{P} \end{aligned}$$

$$\text{Therefore, } P = \frac{TS \times 100}{L \times A} - \frac{100}{A} \quad [\text{Eq 1}]$$

For 168,000 lb steel:

$$L = \frac{[S]}{100} \times 168,000 = 1680 \times [S]$$

$$\text{And } P = \frac{TS \times 100}{1680 \times [S] \times A} - \frac{100}{A} \quad [\text{Eq 2}]$$

And for  $\frac{(S)}{[S]} = 6.0$  and  $[S]$  0.025, 0.030, and 0.035, the calculations are given in the following table:

|                   | For 0.025 Pct Sulphur Steel                                        | For 0.030 Pct Sulphur Steel                                        | For 0.035 Pct Sulphur Steel                                        |
|-------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| Slag wt pct $P =$ | $\frac{TS \times 100}{1680 \times 0.025 \times 6} - \frac{100}{6}$ | $\frac{TS \times 100}{1680 \times 0.030 \times 6} - \frac{100}{6}$ | $\frac{TS \times 100}{1680 \times 0.035 \times 6} - \frac{100}{6}$ |
| Slag wt pct $P =$ | $\frac{TS}{2.52} - 16.7$                                           | $\frac{TS}{3.02} - 16.7$                                           | $\frac{TS}{3.52} - 16.7$ [Eq 3]                                    |

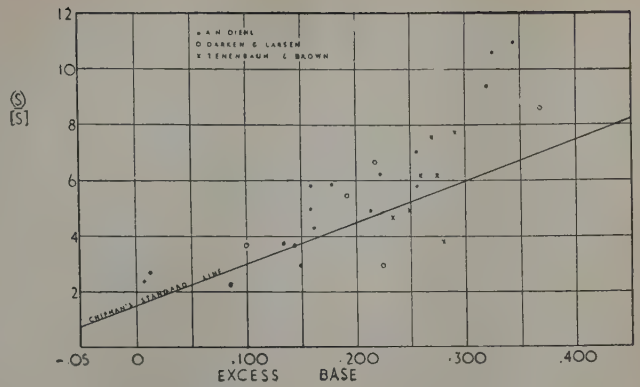


Fig. 9—Sulphur distribution in the basic open hearth. After Chipman and Grant.

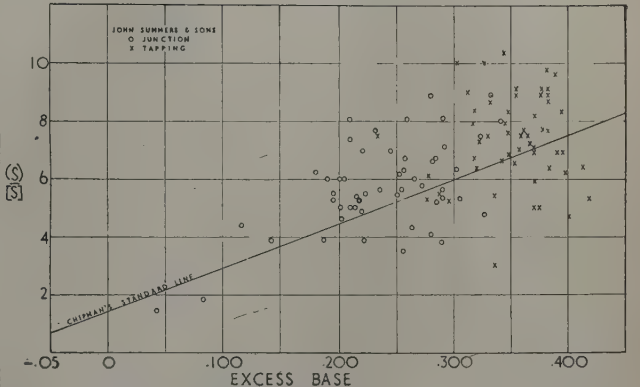


Fig. 10—Sulphur distribution in the basic open hearth. 50 charges. After Chipman and Grant.

Figs. 11a, b, c, and d are charts based upon this calculation, showing the slag weights necessary for 0.025, 0.030, 0.035, and 0.040 pct sulphur steel for differing  $\frac{(S)}{[S]}$  values and pounds of sulphur in steel

and slag. Figs. 12a, b, c, and d are charts for  $\frac{(S)}{[S]}$  values of 4, 6, 8, and 10 showing the slag weights necessary for differing sulphur percentage in the steel and pounds of sulphur in steel and slag. At this stage it only remained to work out simple means to assess the weight of sulphur in steel and slag at junction, and the slag weight increase required between junction and tapping, in order to make the process straightforward enough to be adopted as standard shop practice. Fig. 13 shows the lime additions necessary for the desired slag weight increase.

*Slag Weight:* It can be seen that in order to work such a process, it is essential to be able to estimate the slag weight with reasonable accuracy. In our early work on the experimental furnace, the slag weights were based upon the percentage of phosphorus in the pig iron and the  $P_2O_5$  percentage in the slag. Calculations based upon manganese and lime were also used.

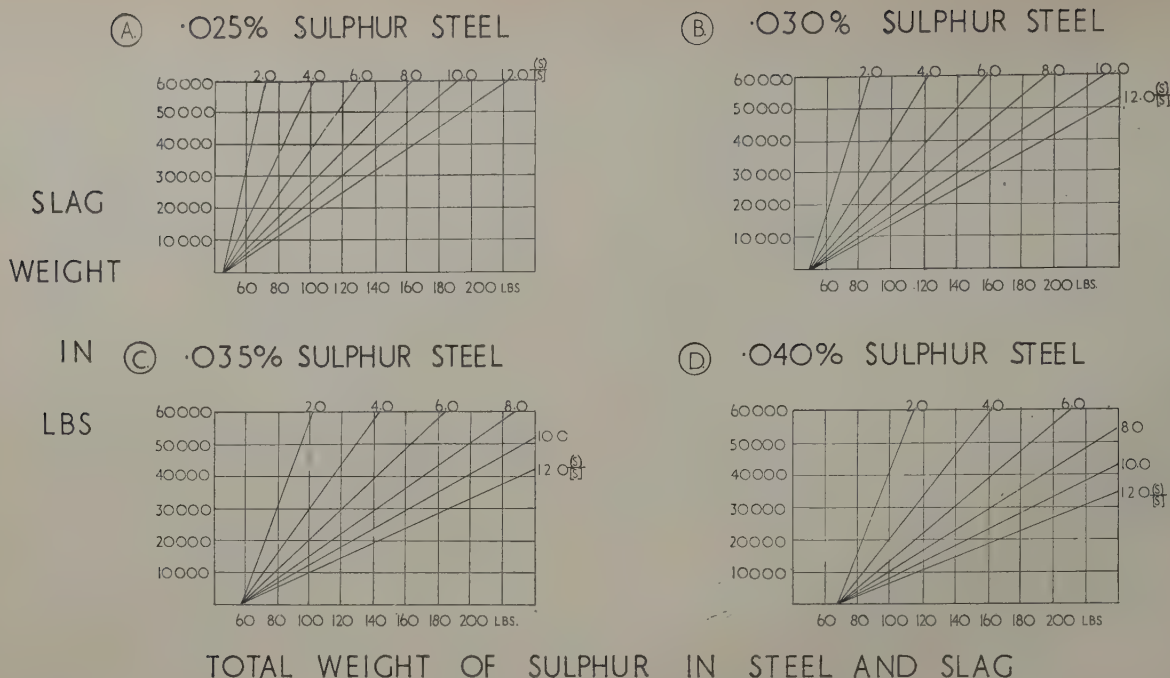


Fig. 11—Slag weight required vs. pounds of sulphur in steel and slag. Steel weight is 168,000 lb.  $\frac{(S)}{[S]}$  is 2.0 to 12.0.

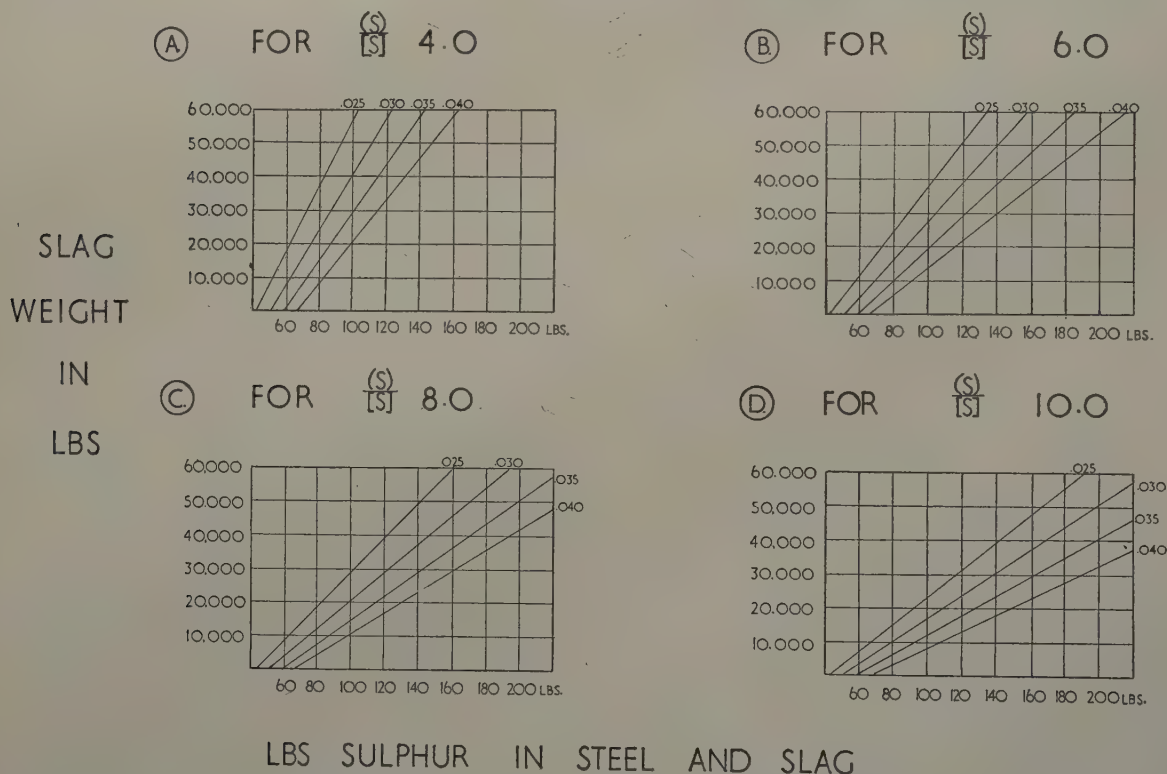


Fig. 12—Slag weight vs. pounds of sulphur in steel and slag. Steel weight is 168,000 lb. Final  $[S]$  pct is 0.025, 0.030, 0.035, and 0.040.

Table II\* gives the result of a comparison of the slag weights obtained when calculated from  $P_2O_5$  and from lime. Also included in this table is the figure by which the final sulphur percentage in the steel would be affected by the error between the two figures for slag weight at junction. Though the actual difference in slag weight appears to be considerable in some cases, the effect upon the sulphur percentage in finished steel is relatively small, the

maximum difference is 0.006 pct S, the average absolute difference is less than 0.002 pct S.

Provided that the slag weight can be estimated to about  $\pm 2$  tons, the process can be worked satisfactorily. The slag weight obtained by lime gives results within these limits and has been adopted as a basis for shop practice.

The simple shop rule has been adopted of doubling the weight of lime charged to obtain the slag weight at junction. Fluxing from the banks in this period is not severe and can be ignored. After junction, the bank erosion is severe and is dependent upon the duration of the refining time. Allowance can be

\* For Tables II and IV order Document 3361 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 in. high on standard 35 mm motion picture film) or \$1.00 for photocopies (6x8 in.) readable without optical aid.



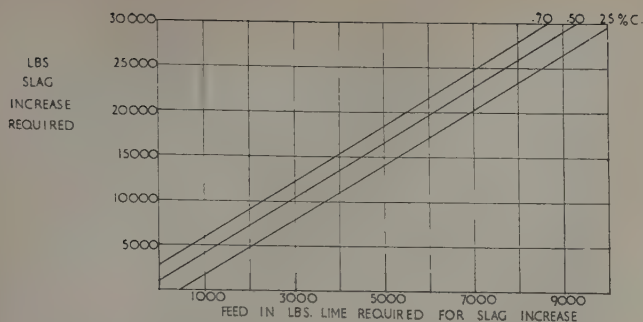


Fig. 13—Lime feed vs. required increase in slag weight.

Furnace capacity is 168,000 lb. Allowance is made for the lime fluxed from the bottom, which is related to the time from junction to tapping. The carbon at junction is used as a measure of the latter.

made for this in calculating the lime addition as shown in Fig. 13 by means of introducing the factor of carbon percentage at junction.

**Rules for Making Steel of a Specified S Content:** The following represent the rules for shop practice reduced to the simplest possible terms:

1—Calculate the weight of pig iron in the charge to give a carbon of 0.3 to 0.5 at junction. This calculation is based on the oxygen equivalent per ton of pig iron as explained for experimental furnace.

2—Calculate the amount of lime to be charged to give a  $V$  value of approximately 4 at junction.

3—Weigh the lime charged to within  $\pm \frac{1}{2}$  ton.

4—Analyze the metal and slag for sulphur at junction and calculate the total weight of sulphur in pounds, assuming the slag weight to be twice that of the lime charged.

5—Calculate the required lime addition from the chart or calculation wheel to give the desired sulphur content at tapping with  $\frac{(S)}{[S]}$  of 6. The maxi-

mum amount of lime that can be fed economically is found by experience. If the weight calculated for the desired sulphur percentage in the steel exceeds this figure, it is advisable to schedule the steel for a higher sulphur percentage and re-calculate the lime required on the new figure.

6—When the carbon is down, the lime in solution, and the temperature 2895° to 2930°F, check the

steel for sulphur percentage and tap the furnace.

**Calculation Wheel:** Fig. 14 shows the calculation wheel for 0.035 pct sulphur steel, and one of these is fitted on to each furnace. From the steel and slag analysis at junction, the weight of sulphur in pounds in each is obtained. From the sum of these, the amount of feed lime required to give 0.035 pct sulphur in the finished steel is read off. This is given in terms of number of barges, each barge being equivalent to 12 cwt (1350 lb) of lime.

Fig. 15 shows a refinement, by which the weights of lime feed required for 0.025, 0.030, and 0.035 pct sulphur steel can be obtained directly from the percentage of sulphur in steel and slag at junction. It must be stressed that the calculation wheel is only applicable for a standard weight of charged lime. A constant weight of 4.7 tons of lime is now used for charges made with the normal supply of pig iron.

**Process in Operation:** It is now 27 months since the process was put into operation on all furnaces in the two shops, and over a million tons of steel have been made during this time. The process is welcomed by the melting shop. All sulphur grades can be made without concern, with scrap, as it comes, either on the oil-fired or gas-fired furnaces. Output has gone up and not down, since its introduction.

It has been said that the process is not accurate enough. It is, therefore, worth looking into the accuracy, to which the shop has to work.

The melting shop manager, ordered to make 0.025 pct sulphur steel, is not held to account if his steel ranges from 0.022 to 0.027 pct.

Fig. 16a, b, c, and d show the effect of errors in slag weight at tapping or  $\frac{(S)}{[S]}$  upon the final sulphur in the steel for a given sulphur burden on a furnace of 168,000 lb steel capacity.

If the case is considered of 100 lb total sulphur burden on Fig. 16b with  $6 \frac{(S)}{[S]}$ , the relative slag weights for 0.022 and 0.027 pct sulphur steel are 46,000 and 34,000 lb. This represents a tolerance of 12,000 lb in the tapping slag weight.

Alternatively, if a slag weight of 42,000 lb is

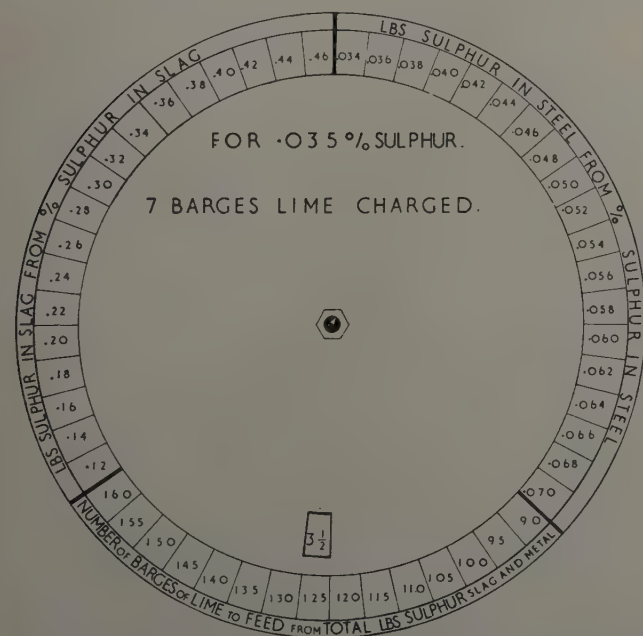


Fig. 14—Furnace calculation wheel for lime to feed for 0.035 pct S steel.

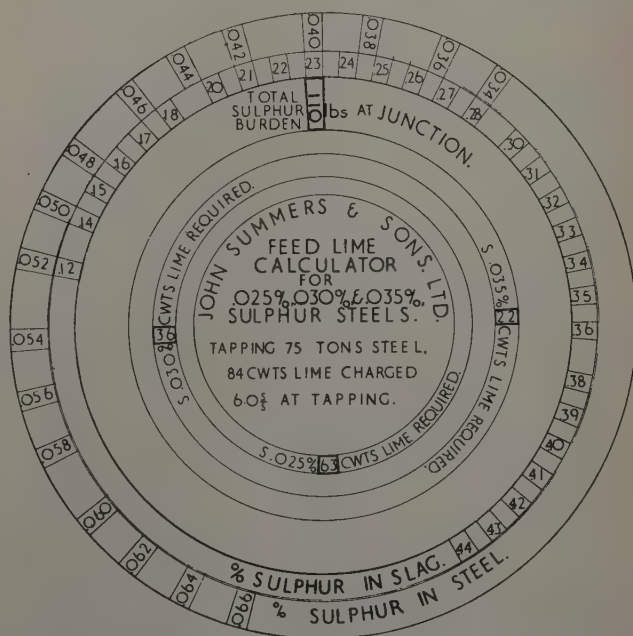
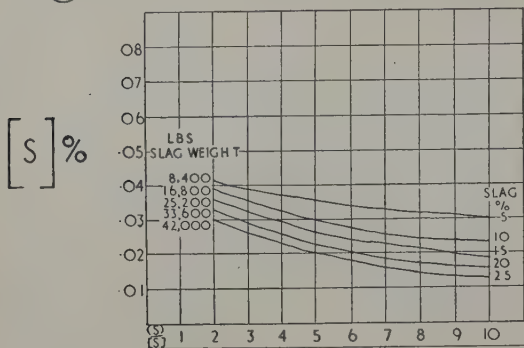
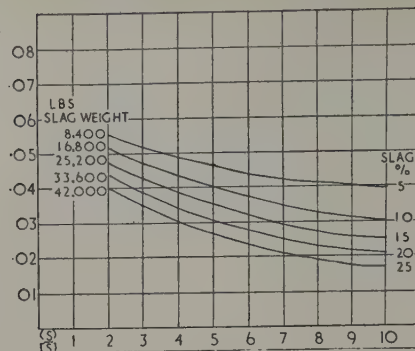


Fig. 15—Calculation wheel for lime to feed for 0.025, 0.030, and 0.035 pct S steel.

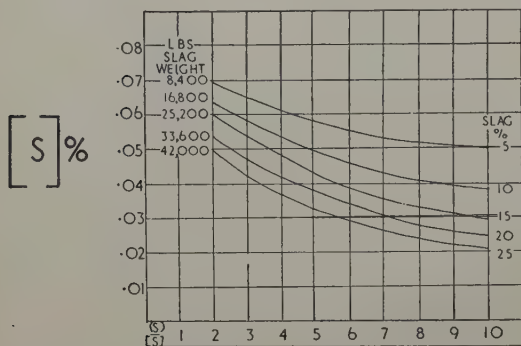
Ⓐ FOR 75 LBS SULPHUR BURDEN



Ⓑ FOR 100 LBS SULPHUR BURDEN



Ⓒ FOR 125 LBS SULPHUR BURDEN



Ⓓ FOR 150 LBS SULPHUR BURDEN

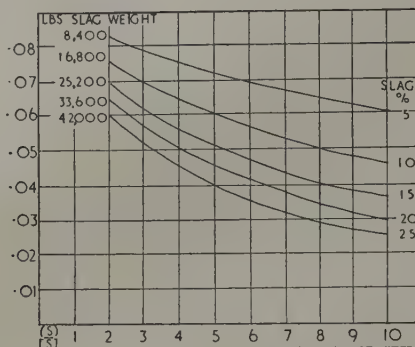


Fig. 16—Effect of varying  $\frac{(S)}{[S]}$  and slag weight on final pct [S]. Steel weight is 168,000 lb.

taken, the difference between 0.022 and 0.027 pct sulphur steel represents a tolerance from 6.8 to 4.8 in  $\frac{(S)}{[S]}$ . The effect of errors of  $\pm 4500$  lb in the slag weight at junction is shown in Table III.

The degree of accuracy that can be obtained is, however, best judged by actual results, and for this purpose we have extracted the results from our No. 2 shop for a period of two months, of all casts made, excluding the first cast of each week, and this is shown in Table IV.\* The comparison between the sulphur percentage ordered and the pit sulphur percentage actually obtained for the same series of casts is shown in Fig. 17.

It will be noted that there is some discrepancy between the calculated and the actual lime additions in certain cases. Where this occurs, the lime fed is, almost invariably, less than the calculated addition. The calculation for the lime addition is based upon a fixed  $\frac{(S)}{[S]}$  at tapping and a fixed amount of lime eroded from the hearth for any particular carbon at junction. If either of these is higher than normal, the amount of lime that need be fed will be less than the calculated figure.

In actual practice in our shops, the latitude allowed in pit sulphur percentage rules the strictness in the pass sulphur percentage before tapping. For instance, when making 0.025 pct sulphur steel, one shop manager allows a furnace to tap after 0.028 pct has been reached with a lapse of 40 min and no further lime addition, provided that the carbon is down to specification even if all the calculated lime has not been added. The manager of another shop feeds all the calculated lime and does no pass tests.

Things will of course tighten up, when the cost office discovers that a 0.020 pct sulphur steel costs more to make than a 0.025 pct steel. The official complaint will then be that the steel is too good for the job and not that it is not good enough.

#### Cost of Making Low Sulphur Steel

The relative slag weights required for making 0.025 pct sulphur steel in a furnace tapping 168,000 lb steel at 6  $\frac{(S)}{[S]}$  are shown by reference to Fig. 11b to be as given in Table V.

Reckoning from yearly consumption of lime and dolomite, the slag weight works out at 20 pct of our ingot production for all grades and over two shops. Steel is manufactured from 0.025 to 0.040 pct sulphur according to the order book. The difference in melting cost (i.e. fuel, reduction in steel, output and furnace repairs) in cash, is not known between our 20 pct slag and the common practice abroad of 8 pct. But on materials alone, the cost of the additional

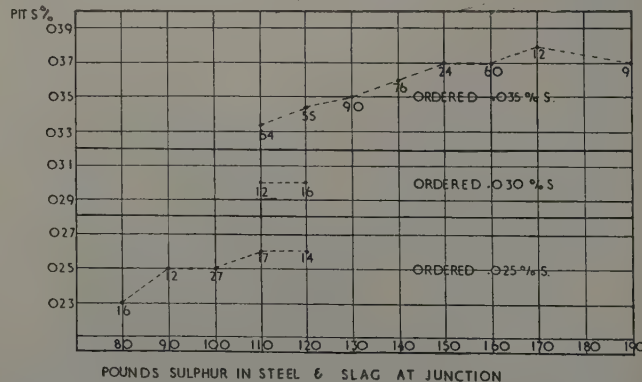


Fig. 17—Summary of results from two months sulphur control, No. 2 shop. Tapping 168,000 lb. Total of 498 casts. The number of casts is averaged under each point.

\* See footnote on p. 1038.



Table III. Effect of Errors of  $\pm 4500$  lb in Slag Weight at Junction

| Slag Weight at Junction, Lb | Junction           |               |                     |                | Tapping    |               |              |                     |
|-----------------------------|--------------------|---------------|---------------------|----------------|------------|---------------|--------------|---------------------|
|                             | S in Slag (S), Pct | S in Slag, Lb | S in Steel [S], Pct | S in Steel, Lb | Total Lb S | Slag Wt in Lb | Slag Wt, Pct | S in Steel [S], Pct |
| 18,800                      | 0.24               | 45            | 0.04                | 66             | 111        | 46,000        | 27.4         | 0.025               |
| 18,800 + 4500               | 0.24               | 55            | 0.04                | 66             | 121        | 50,500        | 30.0         | 0.026               |
| 18,800 - 4500               | 0.24               | 35            | 0.04                | 66             | 101        | 41,500        | 24.7         | 0.024               |
| 18,800                      | 0.36               | 66            | 0.04                | 66             | 132        | 35,000        | 20.8         | 0.035               |
| 18,800 + 4500               | 0.36               | 84            | 0.04                | 66             | 150        | 39,500        | 23.5         | 0.037               |
| 18,800 - 4500               | 0.36               | 51            | 0.04                | 66             | 117        | 30,500        | 18.1         | 0.034               |

lime and iron oxide (which is derived from the metallic iron of the charge) amounts to 8/6 or \$1.30 per ton of steel.

The shop man using high sulphur raw materials and high sulphur fuel has to consider whether the yet unknown melting cost of at least 12 pct or 19,500 lb of slag per cast, added to 8/6 (\$1.30) per ton for material cost, would not justify the spending of a good deal of money to reduce the weight of sulphur in steel and slag at tapping.

### Sources of Sulphur in Steel and Slag

In our cold metal practice, the sources of sulphur weight in the furnace at tapping are as shown in Table VI.

The ways to reduce the weight of sulphur brought in by the pig iron, scrap, lime, spar and dolomite

Table V. Relative Slag Weights for Making 0.025 Pct Sulphur Steel

| Wt S in Steel + Slag at Tapping, Lb | Slag Wt, Lb | Pct Slag Wt of Metal Wt |
|-------------------------------------|-------------|-------------------------|
| 62                                  | 13,500      | 8                       |
| 82                                  | 26,500      | 15                      |
| 93                                  | 33,600      | 20                      |

are so well known technologically that it remains merely a comparison of costs to choose, whether this incoming total sulphur weight is made small, or whether it is left large and desulphurized in the Siemens furnace at the expense of high slag weights.

We are fully aware of the technological ignorance on the one hand, and the possible money saving on the other hand, of reducing the weight of sulphur picked up from, or discharged to, the furnace atmosphere. We can but publish here such data as we have collected, in the hope that it may serve others. Up to the present, we have been quite unable to tie it together into any furnace practice rules.

### Sulphur Pickup from Furnace Atmosphere

The histograms in Figs. 7 and 8, to which reference has already been made, show the spread of sulphur pickup from, or loss to, the furnace atmosphere, that

Table VI. Sources of Sulphur Weight in Furnace at Tapping

|                | Average Weight per Cast, Lb | Sulphur, Pct | Sulphur per Cast, Lb |
|----------------|-----------------------------|--------------|----------------------|
| Pig iron       | 62,800                      | 0.03-0.07    | 19-45                |
| Uprising scrap | 58,200                      | 0.025-0.05   | 15-29                |
| Bought scrap   | 58,200                      | 0.04-0.07    | 23-43                |
| Lime           | 11,250                      | 0.1-0.2      | 11-22                |
| Dolomite       | 6,750                       | 0.1-0.3      | 7-21                 |
| Spar           | 450                         | 0.6-0.8      | 3-4                  |
| Oil            |                             | 2.3-2.6      | -30-+95              |
|                |                             |              | 48-259               |

had been obtained from charges made in the early stages of adoption of our process. Table VII shows the results for all our controlled charges to date.

It will be noted that the pickup, particularly from junction to tapping, has increased markedly from series V. Though other changes have taken place during the period under review, it is very significant that between series IV and V a change was made in our supply of oil. The sulphur content which was 2.4 to 2.5 pct before rose to 2.6 to 2.8 pct after the change. Table VIII shows the partition of sulphur between slag and metal at junction and tapping. It will be noted that there has been a distinct tendency for the  $\frac{(S)}{[S]}$  at tapping to rise in the same way as the pickup of sulphur has risen. Fig.

Table VII. Pounds S Picked Up from (+) or Lost to (-) Furnace Atmosphere from Liquid System Steel and Slag

| Series | No. of Charges | Start Charge to Junction |          | Junction to Tapping |         | Start Charge to Tapping |          |
|--------|----------------|--------------------------|----------|---------------------|---------|-------------------------|----------|
|        |                | Average                  | Range    | Average             | Range   | Average                 | Range    |
| I      | 97             | +31.6                    | -30-+90  | -8.8                | -50-+30 | +22.7                   | -40-+90  |
| II     | 63             | +21.5                    | -20-+70  | -9.8                | -50-+40 | +11.6                   | -30-+70  |
| III    | 51             | +41.3                    | -10-+100 | -13.2               | -60-+30 | +28.1                   | -30-+80  |
| IV     | 38             | +16.1                    | -40-+50  | +4.8                | -30-+40 | +21.0                   | -70-+70  |
| V      | 15             | +35.6                    | +10-+60  | +29.0               | 0-+70   | +64.6                   | +40-+110 |
| VI     | 22             | +30.2                    | +10-+60  | +22.5               | -20-+50 | +52.8                   | +20-+80  |
| VII    | 13             | +43.5                    | +20-+70  | +15.4               | -10-+50 | +58.8                   | +30-+90  |
| VIII   | 32             | +46.9                    | +10-+100 | +18.2               | -30-+60 | +65.0                   | +10-+100 |

18 shows the relation between sulphur pickup between junction and tapping and  $\frac{(S)}{[S]}$  at tapping for a number of individual charges. It can be seen that there is a trend for the high figures for sulphur pickup to be associated with high  $\frac{(S)}{[S]}$  at tapping.

It can perhaps be argued that, if the sulphur passes from the furnace atmosphere to the slag, the sulphur in the slag does not necessarily reach equilibrium with sulphur in the metal, whereas, if the sulphur passes from the metal to the slag, then equilibrium is reached. If there is any truth in this

Table VIII. Partition of Sulphur between Slag and Metal

| Series | Junction |         | Tapping |          |
|--------|----------|---------|---------|----------|
|        | Average  | Range   | Average | Range    |
| I      | 5.8      | 2.3-9.8 | 5.2     | 3.9-8.1  |
| II     | 5.7      | 2.2-8.1 | 6.2     | 3.3-9.3  |
| III    | 5.8      | 1.9-9.8 | 6.8     | 3.0-10.3 |
| IV     | 5.5      | 1.4-8.2 | 7.7     | 4.7-12.2 |
| V      | 5.7      | 2.3-8.9 | 7.8     | 5.6-9.7  |
| VI     | 5.5      | 2.3-8.8 | 8.0     | 5.0-11.2 |
| VII    | 6.2      | 3.2-8.8 | 7.9     | 5.7-9.6  |
| VIII   | 6.0      | 2.1-9.8 | 8.0     | 4.7-11.0 |

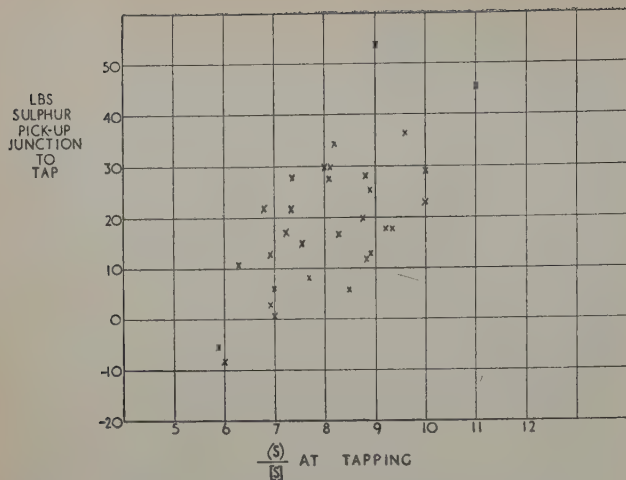


Fig. 18—Relation between sulphur pickup, junction to tap and  $\frac{(S)}{[S]}$  at tapping.

explanation, it would help to explain some of the anomalies found between  $\frac{(S)}{[S]}$  by analysis and by excess base calculations in the high  $\frac{(S)}{[S]}$  range.

It is often stated that reducing conditions tend to favor sulphur pickup, so sulphur pickup has been

Table IX. Influence of Weight of Lime Charged on Sulphur Pickup

| No. of Charges | Wt Lime Charged, Lb | Average Sulphur Pickup   |                 |                     |
|----------------|---------------------|--------------------------|-----------------|---------------------|
|                |                     | Start Charge to Junction | Junction to Tap | Start Charge to Tap |
| 16             | 9400                | 50.0                     | 17.8            | 67.4                |
| 16             | 5380                | 40.9                     | 21.1            | 62.3                |

#### WASTE GAS ANALYSIS SAMPLING LAYOUT

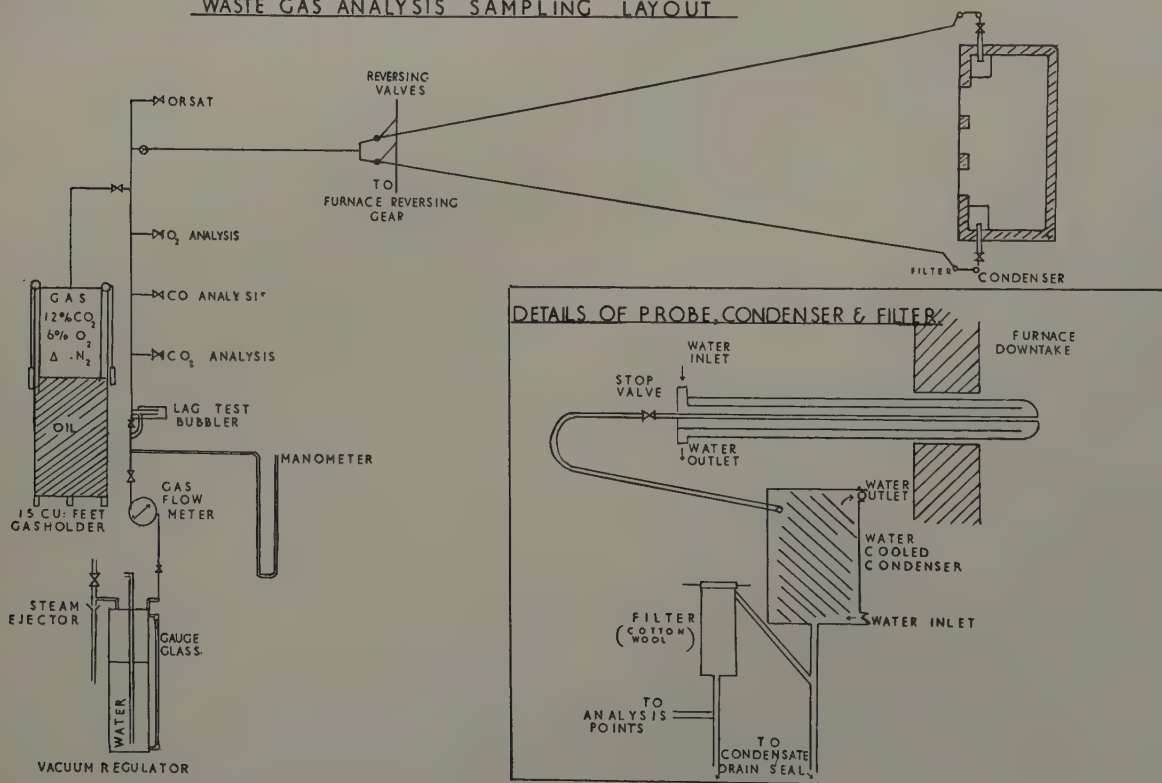


Fig. 19—Layout for continuous waste gas sampling.

plotted against factors likely to influence combustion conditions such as oil flow, steam flow, metered air, percent oxygen in the waste gas, etc., but so far no significant trends have been found. The amount of sulphur pickup from start charge to junction, does however, appear to be influenced by the weight of lime charged. Figures from one series of charges, in which a comparison was made between high and low phosphorus iron, with corresponding high and low weights of lime charged are given in Table IX. The reduced pickup is probably due to rather earlier slag formation and to the reduced amount of lime exposed directly to the flame.

#### Fuel Burning to Control Gas Composition

We have read much and done much work on the furnace control necessary to burn fuel so that the gases sweeping the slag or particular geographic areas of the slag have a particular composition. It seems to us that, much as we want scientists to discover the chemistry of the passage of sulphur between specific mixtures of gases on the one hand, and solid pig, and scrap, solid lime, liquid slags, and liquid steel on the other hand, such knowledge will be of little use, until furnace men can reproduce in the furnace what the scientist may find he wants. Our part of the work may take as long and seem more impossible than theirs, but we think that furnace combustion control must precede any real effort the scientist may make. The stimulus to the scientist will become very real when he knows that we have the tools waiting to apply his discoveries. A start has been made on automatic continuous waste gas analyses and on the control of oil-air ratio on the results.

This problem was divided into two parts: 1—sampling, and 2—the invention of recording automatic analyzer. Sampling is considered to be a furnace fitter's problem and therefore we undertook it ourselves. The instruments were handed over to instrument makers and they were given, at the fur-



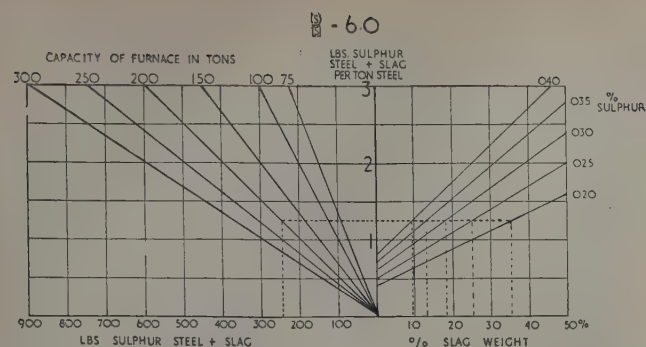


Fig. 20—Slag weights required for varying pounds of sulphur in furnaces of different sizes.

nace, a cool clean place and a pipe through which the gas that was to be analyzed passed at a rapid rate to waste.

The sampling arrangements have been successful for  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$ , for which one sampling tube was used. This is shown in Fig. 19 with the testing apparatus both for the gas tightness of the sampling tube and the testing of the correctness of the gas analysis. These analyses are used on the experimental furnace to control the air screw by human link, but it is hoped that this will be incorporated in the fully automatic furnaces now being built.

A steam-lagged sampling tube for water in gas analysis was built successfully, but the instrument makers have, so far, failed in measuring automatically the water condensed in unit time. A satisfactory sampling method for  $\text{SO}_2$  has not been devised and in addition, we are rather doubtful of any recording automatic analysis for  $\text{SO}_2$ , to operate on an open hearth furnace that has yet come to our notice. The difficulty in sampling is that iron oxide is such a good catalyst for  $\text{SO}_2$ - $\text{O}_2$  reaction and that water is such an excellent absorber of  $\text{SO}_3$ . We feel that some day we will have to return to it.

We are very much aware that the waste gases sampled in the downtake at stage level are not representative of the gases sweeping in the hearth at the middle door and much less at the first door. These are the places that count, and we are at a complete loss for the moment as to how to tackle the practical side of any solution that chemists may put forward. We must remember that it is not the chemists' job to give a practical solution. His job is to tell us the chemistry and it is ours to find the practical solution.

### Conclusion

The process, which has been described, has provided us with a simple calculation that enables us to make steel to the sulphur specification required, from available raw materials. The process has been worked out specifically to meet our particular conditions. We would, however like to suggest that it forms a logical approach to the study of sulphur in the open hearth furnace. There should be no reason why it could not be modified to suit other conditions, in cases where sulphur governs the slag bulk.

The fundamental principle that we wish to stress is consideration of weights of slag, and steel, and of sulphur in each, in addition to the percentages of sulphur in slag and steel. The tacit assumption of so many workers, that the slag weight remains constant, is one that we cannot accept, and we should like to urge other investigators not to omit taking the weights into consideration. Fig. 20 gives the relation between pounds of sulphur in steel + slag and slag weight percentage required, assuming an

$\frac{(S)}{[S]}$  of 6 for different sized furnaces.

### Acknowledgments

This paper is presented as the work of John Summers & Sons. Means had to be found to continue to make low sulphur steel on all furnaces, despite increasing sulphur burden. All departments and organizations threw in their weight to achieve this end. The authors were given the job of organizing the work and are only mentioned as three of the gang at whom the technological public might aim their criticisms. Internal acknowledgments are therefore out of place.

We would wish, however, to thank Sir Charles Goodeve, Director of The British Iron and Steel Research Association (and our other friends in The British Steel Industry) for having allowed members of their staffs to give us so much help. They helped us with statistical work and hours of seemingly unprofitable conference, until one day, we found what we have published just lying on our office table.

Finally one of the authors was given much help by a short conversation with John Chipman and C. H. Herty, Jr. at a scientific conference in England.

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- <sup>3</sup> F. L. Robertson and W. Thring: *Journal British Iron and Steel Inst.* (September 1949) **163**, pp. 31-50.
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### DISCUSSION, H. L. Tear presiding

**S. L. Case** (*Battelle Memorial Institute, Columbus, Ohio*)—What effect does the control of slag weight have on the production? If there is high sulphur in the charge at the start, there will be a high slag weight in order to meet the low sulphur specifications. What effect will this have on production?

**C. H. Bacon** (authors' reply)—That is rather a difficult question to answer satisfactorily. Production rate has gone up since we introduced the process, and it enables us to make the required lime additions early. We carried out a trial to compare the use of American low sulphur and phosphorus pig iron with our normal supply and we were able to show a reduction in slag weight and an appreciable increase in production rate. I think I can say we could work faster if we could keep the slag weight lower.

**H. L. Tear** (*Jones & Laughlin Steel Corp., Pittsburgh*)—Our answer to that, Mr. Case, is much different than Mr. Bacon's. It has a great deal of influence on production rates. Fig. 21 shows the lime consumption with the different specifications of sulphur; 80 pct of the heats are in the 0.025 S range and the effect of lower sulphur on lime consumption can be seen. Fig. 22 shows that, with different preliminary sulphur ranges, taking 0.04 as the base, as the first sulphur test goes up there is a loss in production rate, as indicated. With a preliminary sulphur of 0.071 or over, the production rate loss is in the neighborhood of 8 pct, which is much different from that reported by Mr. Bacon.

**Mr. Bacon**—I should just explain, Mr. Tear, that we have never had an opportunity to work with such low slag weights as you carry over here.

**C. R. Funk** (*American Locomotive Co., Latrobe, Pa.*)—Will you give us something on the rates?

**Mr. Bacon**—We have a small furnace and our rate of work is approximately 7.3 tons per hr, or 55 lb per sq ft of hearth area.

**Mr. Tear**—How many pounds of fluorspar?

**Mr. Bacon**—We use an average of 2 or 3 cwt of spar with the charge of 84 tons.

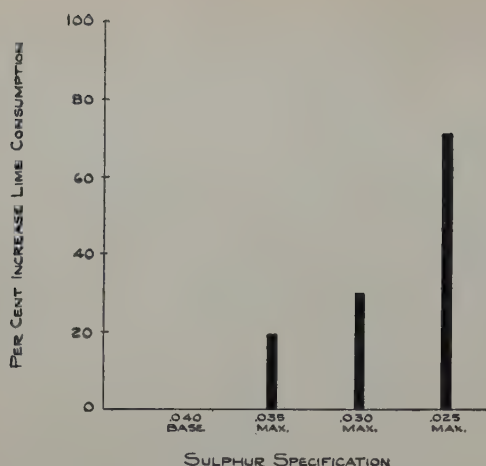


Fig. 21—Sulphur specification vs. lime consumption.

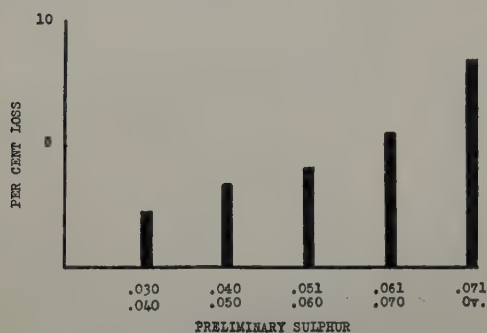


Fig. 22—Preliminary sulphur vs. production loss.

**Mr. Tear**—You add roughly 330 lb of spar per ton?

**Mr. Bacon**—No, per charge, about 3 lb per ton.

**Mr. Tear**—In our case it is around 14 lb of spar per ton of ingots with a slag rate of about 300 lb per ton.

**W. A. Peters** (*Laclede Steel Co., Alton, Ill.*)—How do you get the higher S over S value. If you want it up higher what do you do about getting it up there?

**Mr. Bacon**—The higher S over S values that we showed toward the end were our later charges and we assumed it to be due to the fact that we had a higher proportion of sulphur in the furnace atmosphere and a higher pickup of sulphur to the slag from the furnace atmosphere.

**L. S. Darken** (*U. S. Steel Co., Kearny, N. J.*)—If the sulphur burden is high at junction so that greater lime addition is required, it seems that this would increase the sulphur distribution ratio. The extra time as well as the lime might be expected to increase the sulphur pickup. Thus the correlation between distribution ratio and pickup may be indirect.

**Mr. Bacon**—I do not think we have any figures to show that the sulphur pickup is greater, when more lime is fed.

**C. E. Sims** (*Battelle Memorial Institute, Columbus, Ohio*)—Would the fact that the S over S ratio does increase with sulphur pickup indicate you probably did not have equilibrium between metal and slag? You have mentioned that you thought you did have equilibrium. This might indicate you did not.

**Mr. Bacon**—The suggestion is, that, if the sulphur is coming into the slag from the furnace atmosphere, we probably do not reach equilibrium between slag and metal, but if it is coming from the metal into the slag we are more likely to reach equilibrium.

**W. T. Sergy** (*Jones & Laughlin Steel Corp., Pittsburgh*)—This junction seems to be in every correlation that you make and if I understand correctly a definite bath temperature is desirable at a certain carbon. Do you have any limits or range for bath temperature, or do you aim at one particular temperature for a certain carbon content of the bath?

**Mr. Bacon**—We aim at 0.3 to 0.5 pct C at junction. If we melt out at 0.9 pct C, we want a temperature of 1510°C; at 0.4 pct C, 1560°C.

**Mr. Sergy**—Does every heat have a junction?

**Mr. Bacon**—Yes.

**Mr. Sergy**—Suppose at 38 or 40 pct C you do not have the proper temperature?

**Mr. Bacon**—We do not call that junction from the point of view of taking samples.

**Mr. Sergy**—Do you add lime or any other flux on such a basis?

**Mr. Bacon**—No, we wait until we pick up the temperature and then we take the junction.

**Mr. Sergy**—And if you never get it?

**Mr. Bacon**—We have to pick up the temperature to attain a minimum temperature at tapping.

**Mr. Sergy**—What I am trying to resolve is, do you make any calculations on the amount of lime you would add when you do not have a junction?

**Mr. Tear**—I think Mr. Sergy means, if you get to the point where you have to refigure a heat do you apply this practice to that heat in the case of a soft melt?

**Mr. Bacon**—In the case of a very soft melt, we cannot always add enough lime to reach specification.

**Mr. Sergy**—When junction is not obtained due to too high a bath temperature, do you still make your calculations on that basis?

**Mr. Bacon**—If the temperature is high at the junction we can feed rapidly.

**Mr. Sergy**—And if you are low, you do not?

**Mr. Bacon**—If we melt very soft, we do have to anticipate the junction.

**W. O. Philbrook** (*Carnegie Institute of Technology, Pittsburgh*)—Have you had time to apply the waste gas analysis, and if so has any trend of variation of the sulphur pickup with the oxidizing potential of the atmosphere been noted?

**Mr. Bacon**—We have tried to obtain a relation but have failed so far. We have been using an absorption type of analyzer, which is not altogether satisfactory as it involves a delay of about 4 min. We have now installed a paramagnetic type of meter with a quick response. We shall check this on future charges.

**T. S. Washburn** (*Inland Steel Co., Chicago, Ill.*)—It would be interesting to know whether these relations vary with the carbon content of the bath: for example, 0.60 pct C as compared with 0.10 pct C.

**Mr. Bacon**—The data are all from low carbon steel.

**Mr. Washburn**—Consequently, the relations would not be the same for medium or high carbon.

**R. L. Long** (*Carnegie Institute of Technology, Pittsburgh*, and also from an English steel firm, *The Park Gate Iron & Steel Co., Ltd., Rotherham, England*)—There are two questions I wish to ask. First of all, is your sulphur determination equally rapid, and what is its accuracy? Second, you have mentioned a temperature carbon line for your junction. Is that based on a given superheat, say according to the carbon, or is it based on your own experience as to the suitable stage at which to commence feeding the charge?

**Mr. Bacon**—As regards the accuracy of the rapid sulphur determination in slag at junction, we consider it to be of the order of 5 or possibly 10 pct. On a slag of 0.22 pct S, the rapid method should give a figure between 0.21 and 0.23.

**Mr. Tear**—How did you arrive at the origin of the carbon temperature line?

**Mr. Bacon**—That was arrived at by experience on the furnace.

**Mr. Funk**—What is the depth of the bath? What do you do when you have a furnace that does not work very well? Is there a difference between a sharp working furnace and a sluggish working furnace?

**Mr. Bacon**—The depth of the bath is about 2 ft 6 in. for an 80 ton furnace. A sluggish furnace tends to pick up more sulphur than a sharp working one, but the greater part of this occurs before junction, so the analysis at junction should take care of that.



# Discussion — Extractive Metallurgy Division\*

St. Louis Meeting, February 1951

|                                                                                                                                                               |      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Sintering Practice at Josephtown Smelter (paper by H. K. Najarian, K. F. Peterson, and R. E. Lund. JOURNAL OF METALS, February 1951, p. 116).....             | 1045 |
| Arc Melting of Titanium Metal (paper by S. F. Radtke, R. M. Sriver, and J. A. Snyder. JOURNAL OF METALS, August 1951, p. 620).....                            | 1046 |
| Thermodynamics of Iron-Silicate Slags: Slags Saturated with Gamma Iron (paper by R. Schuhmann, Jr. and P. J. Ensio. JOURNAL OF METALS, May 1951, p. 401)..... | 1046 |
| Metallurgical Reactions of Fluorides (paper by H. H. Kellogg. JOURNAL OF METALS, February 1951, p. 137). ..                                                   | 1046 |

\* TP 3173D. Since some of the annual meeting papers had not been published sufficiently in advance of the time this discussion went to press, discussion of these papers will appear when discussion is published next spring.

## Sintering Practice at Josephtown Smelter

by H. K. Najarian, Karl F. Peterson, and Robert E. Lund

DISCUSSION, T. H. Weldon presiding

**R. E. Powers** (Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh)—Several of the processing methods at the Josephtown smelter might well be considered by plants producing iron blast furnace sinter. In making blast furnace sinter the objectives are much the same as at Josephtown: To produce a strong yet porous agglomerate which has a size consist in a preferred range. The emphasis however is on production rate rather than on the size or other quality characteristics of the sinter. Therefore the technique is entirely different. Blast furnace sinter plants attempt to make their product in one pass with a minimum recirculating load and without sizing treatment after the sinter leaves the machines. Many plants are beginning to feel that more attention paid to quality characteristics would make the product a more desirable blast furnace material.

The pelletizing of very fine material before placing it on the bed is not deliberately done at iron sinter plants, although the installed equipment sometimes gives a similar action. Such pelletizing seems to be a promising way of accommodating the down-draft sintering process to very fine materials.

The recirculating load at Josephtown is extremely high. Two plants<sup>1</sup> producing blast furnace sinter from raw material of comparable size have a recirculating load of about 100 pct of production. At Josephtown it is notable that the size and the rate of feeding of return fines are under control. This is not the case in most blast furnace sinter plants. The sinter slicer appears to be a worthwhile aid in effecting such control. It is similar in action to rakes and plows used at a number of plants, but it has the advantage that the sinter dislodged is positively removed and not left to the inefficient action of a stationary grizzly screen.

Blast furnace size specifications for sinter are not at present so rigid as the Josephtown specifications. If the sizing of blast furnace sinter does become important, then the Josephtown crushing practice, in which a large recirculating load is maintained on the crusher in order that minimum fines be produced, may be of interest.



Fig. 2—Feed to Dwight and Lloyd sinter machine, Josephtown Smelter.

**H. K. Najarian** (authors' reply)—We note that Mr. Powers appreciates some points that we tried to emphasize in our paper as being of importance in making zinc sinter of good quality and which may well be applied to iron blast furnace sinter.

Fig. 2 shows the pelletized nature of the feed going on to a Dwight-Lloyd type sintering machine in our plant. Practically, the entire feed consists of more or less rounded particles which permit more uniform air passage through the charge, while the larger particles in the charge roll on to the surface of the grate, which helps to keep the grate openings from being clogged by excessive fines. An agglomerated charge of this character may preferably be made by rolling action while being mixed in a rotating drum and wetted by water sprays to bind the fine particles together and give the charge the desired moisture content. From our observations of several iron ore and blast furnace flue dust sintering operations, we believe that if the fines from the sinter discharged from the machines were to be recirculated and agglomerated with the new feed, not only sinter of better quality but larger capacity from the machines may be realized.

<sup>1</sup> R. R. Burns: Operation and Practice, Producing Iron Sinter at Ducktown and Copperhill, Tennessee, with Fine Flotation Sulphides. Blast Furnace Coke Oven and Raw Materials Committee Proceedings. AIME (1949) 8, pp. 146-150.

# Arc Melting of Titanium Metal

by S. F. Radtke, R. M. Sriver, and J. A. Snyder

## DISCUSSION, J. R. Long presiding

**R. I. Jaffee** (*Battelle Memorial Institute, Columbus, Ohio*)—The authors have written a fine and important paper, and are to be congratulated. I do not entirely follow their discussion of the relationship between the ductility of titanium and its crystal structure. Since high purity titanium is extremely ductile, being capable of cold reductions of over 99 pct, its ductility cannot be unduly restricted by its hexagonal crystal structure. It is true that interstitial solid solutions of nitrogen and oxygen do have a restricting effect on ductility, but this would appear to be an alloying effect rather than a crystal structure effect. The point made by the authors concerning the relative ductility between forged and rolled titanium does not appear to be conclusive, either. It would appear that in the same condition forged material would have equivalent or better ductility than sheet material. The difference between the ductility reported for forged bar and annealed sheet in Table I may be the result of a greater degree of cold work in the as-forged condition.

**S. F. Radtke, R. M. Sriver, and J. A. Snyder** (authors' reply)—We appreciate the discussion by Dr. Jaffee. His point is well taken that the hexagonal structure of titanium does not, in itself, restrict the ductility of iodide material and, therefore, should not be limiting in this case. It is true, however, that the ductility of different grades of titanium is not necessarily related to their hexagonal structure but more likely to their orientation and composition. It is also true that the presence of small amounts of foreign elements in hexagonal metals may have more pronounced influence on ductility than a corresponding quantity in cubic metals.

Average values from a large number of tests might show relatively better ductility for forged titanium than is recorded in Table I. The forged bars used in this work were tested in the annealed condition; little is known concerning the effect of forging practice on ductility in titanium metal.

## Thermodynamics of Iron-Silicate Slags: Slags Saturated with Gamma Iron

by R. Schuhmann, Jr. and P. J. Ensio

### DISCUSSION, N. Arbiter presiding

**John Chipman** (*Massachusetts Institute of Technology, Cambridge, Mass.*)—The activity of FeO in silica-saturated slags shown in Table V is about 0.40 in the temperature range 1260° to 1350°C. Recent

measurements by N. A. Gokcen at 1600° lead to about the same value. He finds the oxygen content of liquid iron in equilibrium with silica and ferrous silicate slags to be 0.088 pct. Under pure iron oxide slags at the same temperature, it is 0.225 pct. The ratio places the activity at 0.39.

## Metallurgical Reactions of Fluorides

by Herbert H. Kellogg

**C. M. Decroly** (*University of Brussels, Belgium*)—The importance of the fluorides in the process metallurgy of special metals has already been accepted and it will probably increase in the future. Free energy diagrams as such established by Professor Kellogg are therefore very useful.

It is interesting to note that the absolute value of the standard free energy of formation of HF increases with temperature, whereas for almost all the other fluorides it decreases; consequently it should be theoretically possible to reduce all the fluorides of the metals which, at low temperature, have a greater affinity for fluorine than hydrogen by this last element, provided a sufficiently high temperature is used in order to have a good efficiency.

However, with regard to the reduction of UF<sub>6</sub> by hydrogen, I doubt that it will be possible to obtain directly the metal at comparatively low temperatures. There are other uranium fluorides which are more stable than UF<sub>6</sub> and it is very likely that such fluorides will be obtained first. For example, in considering the reaction:



it is found, using the thermodynamic data of Brewer et al, that  $\Delta H_{298} = -66$  kcal and  $\Delta G_{298}^{\circ} = -65.2$  kcal.

As a result, the reduction of UF<sub>6</sub> to UF<sub>4solid</sub> should proceed spontaneously even at ordinary temperature. On the other hand, the standard free energy of formation of UF<sub>4solid</sub> at 298°K is  $\Delta G_{298}^{\circ} = -209$  kcal per mol of F<sub>2</sub>. The reduction of UF<sub>4</sub> by hydrogen will be practically difficult and, as it is known, the only practical way of reducing this compound is to use alkaline-earth metals such as calcium or magnesium. I should like to point out, further, that the fluorination of many metal oxides can be carried out very easily by using the ammonium difluoride method of preparation, which renders the use of fluoride gas unnecessary. The first compound formed is generally a double fluoride of the metal and ammonium. This compound can be decomposed by heating either in a vacuum or in an inert atmosphere, ammonium fluoride being volatilized leaving the metal fluoride in a very pure state.

**H. H. Kellogg** (author's reply)—Professor Decroly is quite right in pointing out that the formation of lower halides of uranium may complicate the reduction of UF<sub>6</sub> by H<sub>2</sub>. I was unable to find his reference to the free energy of formation of UF<sub>4</sub> in the compilation of Brewer,<sup>13</sup> however. The value of  $\Delta G_{298}^{\circ} = -209$  kcal for formation of ½ UF<sub>4</sub> seems rather high, and I hope the source of this value may be made clear.



# Discussion — Iron and Steel Division\*

St. Louis Meeting, February 1951

|                                                                                                                                                                                                                                                    |      |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| A Thermodynamic Study of the Reaction $\text{CaS} + \text{H}_2\text{O} \rightleftharpoons \text{CaO} + \text{H}_2\text{S}$ and the Desulphurization of Liquid Metals with Lime (paper by T. Rosenqvist. JOURNAL OF METALS, July 1951, p. 535)..... | 1047 |
| Effects of Manganese and Its Oxide on Desulphurization by Blast-Furnace Type Slags (paper by N. J. Grant, U. Kalling, and J. Chipman. JOURNAL OF METALS, August 1951, p. 666).....                                                                 | 1048 |
| Effect of Silica Reduction on the Desulphurizing Power of Blast-Furnace Type Slags (paper by N. J. Grant, O. Troili, and J. Chipman. JOURNAL OF METALS, August 1951, p. 672).....                                                                  | 1049 |
| Distribution of Sulphur Between Liquid Iron and Slags of Low Iron-Oxide Concentrations (paper by R. Rocca, N. J. Grant, and J. Chipman. JOURNAL OF METALS, April 1951, p. 319).....                                                                | 1050 |
| Desulphurizing Molten Iron with Calcium Carbide (paper by S. D. Baumer and P. M. Hulme. JOURNAL OF METALS, April 1951, p. 313).....                                                                                                                | 1051 |
| Desulphurization of Pig Iron with Pulverized Lime (paper by B. Kalling, C. Danielsson, and O. Dragge. JOURNAL OF METALS, September 1951, p. 732).....                                                                                              | 1052 |
| Kalling-Domnarfvet Process at Surahammar Works (paper by S. Fornander. JOURNAL OF METALS, September 1951, p. 739).....                                                                                                                             | 1052 |
| Low Sulphur Steel from High Sulphur Raw Materials and Fuel (paper by F. L. Robertson, C. H. Bacon, and J. W. Till. Discussion is printed with the paper. This issue, p. 1031).                                                                     |      |
| Solution Loss and Reducing Power of Blast Furnace Gas (paper by T. L. Joseph. JOURNAL OF METALS, January 1951, p. 37).....                                                                                                                         | 1053 |
| Oxygen in Liquid Open-Hearth Steel—Oxidation during Tapping and Ladle Filling (paper by T. E. Brower, J. W. Bain, and B. M. Larsen. JOURNAL OF METALS, June 1950, p. 851).....                                                                     | 1054 |

\* TP 3172C. Since some of the annual meeting papers had not been published sufficiently in advance of the time this discussion went to press, discussion of these papers will appear when discussion is published next spring.

## Thermodynamic Study of the Reaction $\text{CaS} + \text{H}_2\text{O} \rightleftharpoons \text{CaO} + \text{H}_2\text{S}$ and the Desulphurization of Liquid Metals with Lime

by Terkel Rosenqvist

DISCUSSION, W. O. Philbrook presiding

**J. Chipman** (Massachusetts Institute of Technology, Cambridge, Mass.)—The fact that the experimental work has been applied to copper rather than iron and that the paper is presented to the Iron and Steel Division, I regard as rather significant. It shows the unity of metallurgy and the fallacy of trying to cut it up by metals. This result for the solubility of sulphur in molten copper correlates with Professor Schuhmann's finding that the published data on the other side of the copper-sulphur miscibility gap are also in error. I should like to ask the author to say a little bit more about the sulphur capacity of the slag.

**T. Rosenqvist** (author's reply)—I hope that Dr. Chipman will find the derivation of the expression for sulphur capacity more clearly explained in the printed version of the paper than in the oral discussion at the meeting. I feel that this quantity, which actually is the ratio of two activities, can be measured more easily than the individual activities. Even if the ratio  $\text{CaO}/\text{CaS}$  is chosen as the standard state, the expression can be used for any slag, even for slags completely free of lime, and it represents a way to put the desulphurizing power of all slag constituents into one bag.

Some doubt has been expressed as to whether oxygen ions really exist in calcium oxide and in molten slags. From a thermodynamic view point that question is of minor importance. The term oxygen ion activity, or any activity for that matter, is defined rigorously by the equation:  $\text{activity} = \exp \mu/RT$ , where  $\mu$  is the change in free energy connected with the transfer of one mol of ions from the standard state into the slag. Whatever happens to the ion in the slag is of no concern to the thermodynamicist. Regardless of whether the ion is "free" in the slag or not, or whether it is present in a very small amount, its activity can always be expressed, and for a thermo-

dynamic calculation that is all we need. However, ionic activities will only be of some real value if they are simple functions of the slag composition, or can be measured easily.

Concerning the real nature of the oxygen in the slag, my feeling is that the oxygen atom has a rather multiplex nature depending on how strongly it is tied by covalent forces or polarized by the other atoms or ions present. The oxides of iron, cobalt, and nickel differ from calcium oxide and blast furnace slags as to the amount of free electrons that can give rise to electronic conductivity. In slags we know that the conductivity is mostly ionic. The fact that reversible emf's can be obtained with oxygen electrodes in certain salt melts, indicates a significant amount of oxygen ions in these melts. But extended work, e.g. polarographic studies and measurements of transference number, are needed to obtain quantitative information about the real structure of the slags.

**D. E. Babcock** (Republic Steel Corp., Youngstown, Ohio)—With reference to the ion, it might be well to remember Dr. Moses Gomborg. All of his life he had no use for the ionization theory and he contributed greatly to the field of chemistry on the assumption there was no such thing as ions. I do not think we have to worry about whether the oxygen is ionic or not. I think one thing specifically should be brought to your attention and this I think is one of the important contributions of Dr. Rosenqvist. He pointed out what we know as oxygen potentials or what is described as oxygen potentials. I have used this concept for a long period of time and I want to state that if this concept is properly applied, it vitiates much of what we have in the literature, or makes our usual ideas regarding oxidation seem primitive. That one thing is more valuable than almost all the rest of the discussion as a fundamental basis on which to build a reasonable in-

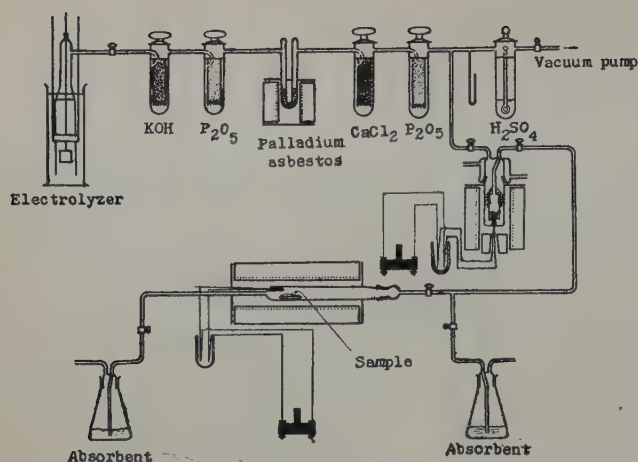


Fig. 9 (above) — Apparatus used in studying the reaction between calcium oxide and hydrogen sulphide.

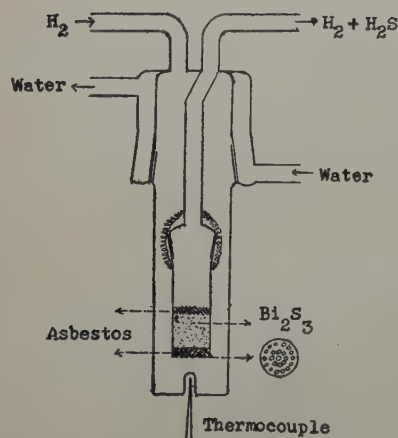


Fig. 10 (left) — Apparatus used to prepare hydrogen and hydrogen sulphide mixed gas.

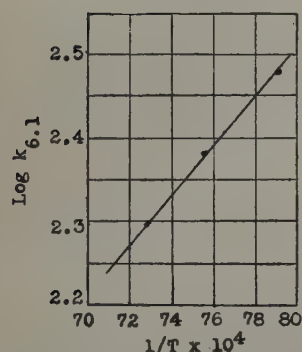


Fig. 11 — Effect of temperature on the equilibrium constant.

terpretation of some of the oxidation phenomena which up to date are poorly interpreted.

It is interesting to bring up another point that Dr. Rosenqvist mentioned about the hydrogen sulphide-water equilibrium, etc. He mentioned the blast furnace in passing. The data of Dr. Darken and some

others indicated that as the moisture went up in the blast furnace, sulphurization was somewhat better. I have been told it is a statistical phenomenon, but it stirs up one's curiosity to do a little looking around relative to the reason that this fact has existed. We do not have anything like the whole answer to this.

If you use the concept of the saturation point of slag and compute the kinetics in the blast furnace, you find if the blast furnace is operated like the laboratory experimental runs, it would not produce. It is interesting and there is more to look at than appears on the face of the data. We have looked so long at the slag, many of us are blinded by the fact that from 75 to 90 pct of all the desulphurization occurs before metal is in contact with a liquid slag.

**Tatsuji Uno** (*Hokkaido University, Sapporo, Japan*) — I have been studying the desulphurization reactions of iron and steel for many years, and finished the study on  $\text{CaO} + \text{H}_2\text{S} \rightleftharpoons \text{CaS} + \text{H}_2\text{O}$  several years ago, but had not been able to publish it, because of the difficulty of printing during and after the war. Fortunately, I could publish it in the *Journal of Iron and Steel Institute of Japan* (*Tetsu to Hagane*), January 1951.

The apparatus used is shown in Fig. 9. Passing the mixture of  $\text{H}_2\text{S}$  and  $\text{H}_2$  over  $\text{CaO}$  and regarding the difference of  $\text{H}_2\text{S}$  content in the gas mixture before and after the reaction as  $\text{H}_2\text{O}$  formed, the equilibrium constant for this reaction was calculated as  $K = p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{S}}$ .

When  $\text{H}_2$  gas passes through  $\text{H}_2\text{S}$  producer shown in Fig. 10, a mixture of  $\text{H}_2\text{S}$  and  $\text{H}_2$  of desired composition is obtained by heating  $\text{Bi}_2\text{S}_3$  at the proper temperature. Therefore, it can be said that my experiment was carried out from the opposite side compared to Dr. Rosenqvist's. I obtained following results from 1000°C to 1100°C:

$$\log K = 3231.8/T - 0.060 \text{ (Fig. 11)}$$

As I used transparent quartz tube, it was difficult to make determinations above 1100°C, and the amount of  $\text{H}_2\text{S}$  at 900°C, was so small, that the experimental errors had largely affected the results. For these reasons, my experiment was limited to a small temperature range.

But I am much pleased to find that your results, obtained over a wide temperature range, are in good agreement with mine.

**Dr. Rosenqvist**—It is a great pleasure to see that Dr. Uno, with a different technique, has arrived at equilibrium values very close to those obtained in my investigation. In the temperature range 1000° to 1100°C the two sets of values differ by 100 cal or less, which is as good as one can expect in work of this kind. The fact that Dr. Uno has approached the equilibrium from the opposite side as compared to my work, shows that true equilibrium has been obtained.

It is only regrettable that the publication of Dr. Uno's work has been delayed so his data were not earlier brought to my attention.

## Effects of Manganese and Its Oxide on Desulphurization by Blast-Furnace Type Slags

by Nicholas J. Grant, Ulf Kalling, and John Chipman

### DISCUSSION, D. C. Hilty presiding

**D. E. Babcock** (*Republic Steel Corp., Youngstown, Ohio*)—I would like to know what evidence you have to prove the  $\text{MnO}$  was pure  $\text{MnO}$ . I would also like to know whether you might not explain it on the basis of a temperature reversion; and, was it due to the oxidizing power of  $\text{MnO}$ ?

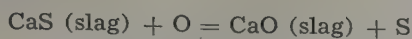
**N. J. Grant** (authors' reply)—Briefly, we have no proof that pure  $\text{MnO}$  was used. The manganese oxide was added as chemically pure  $\text{MnO}_2$ .  $\text{MnO}$  is assumed as the oxide in the reacted slag following standard

molecular slag theories, especially under the reducing conditions of these experiments. The noted sulphur reversion cannot by any means be explained on the basis of a temperature reversion since the temperature effect is shown in this paper to be very small. Until a more logical explanation can be offered, backed I hope by some experimental proof, we propose to explain this sulphur reversion as stated in the paper, namely, that it is due to the oxidizing effect of the added manganese oxide.

**Member**—How did the oxygen in the slag give you a reversion of sulphur? What was the mechanism there?



**Dr. Grant**—One of the simpler possible explanations is that the oxygen replaces the sulphur in calcium sulphide, for example. The reaction might be written as follows:



**Dr. Babcock**—This paper was entitled in relation to blast furnaces. The inference was made that it is a laboratory analogy of a blast furnace process.

**Dr. Grant**—That is exactly what was intended.

**Dr. Babcock**—I think that is not a good idea because it gives us a notion that some things happen in a blast furnace that just do not happen. For example, we get results in a blast furnace that do not fit this picture. You say calcium oxide is several hundred times or so, as effective as MgO. Is that correct?

**Dr. Grant**—That is right.

**Dr. Babcock**—We can, by statistical methods, operate on plant data to determine what the effect is, pretty closely. It is not of that order of magnitude.

The next thing that is of interest is the fact that MgO is in a slag system in which perhaps the physical chemical equilibrium between the associated groups would lead to the conclusion that MgO at any other time could by simple mass effect displace the lime from combination with the other ions or molecules, or whatever you have, so that to discriminate and infer that the effect is only due to lime and not due to lime displacing magnesia in certain systems, I think would be false.

It has been a serious problem to tie together the data of Mr. Hatch, where he figured in his report published by the AIME that the mol for mol excess equivalent effect of magnesia as compared to lime was on the order of two-thirds. Now, we have a ratio of a couple of hundred. The difference of two-thirds effective as lime and a couple of hundred, is a wide gap. Would you put those two things together?

**Dr. Grant**—Such evidence of the superior desulphurizing power of CaO over MgO, notwithstanding manipulated statistical data, is presented in this paper in graphical form, and was also shown for the Hatch and Chipman<sup>8</sup> data in a recent paper by Sherman and Grant.<sup>9</sup> The results from these two different sets of data are in full agreement. The thermodynamic substantiation of the vastly superior desulphurizing power of CaO compared to MgO is noted in the 1600°C equilibrium constants recently calculated by Chipman (*Basic Open Hearth Steelmaking*, Chap. XVI, 2nd Edition, 1951, AIME), and reported in the work of Rocca, Grant and Chipman.<sup>8</sup>

**B. M. Larsen** (*U. S. Steel Co., Kearny, N. J.*)—On the practical effect of MgO on sulphur we propounded some data and Kennedy did some work after that, and we found other data later on. All seem to agree that up to around 6 or 8 pct MgO in the slag, the sulphur ratio increased and above that it seemed to fall off again. From that we inferred that the probable effect of MgO was mainly to give more fluidity to the slag and perhaps thus increase the reaction rate.

**Dr. Grant**—I think that in the case of actual blast furnace work, where the fluidity of the slag and the degree of mixing can be extremely important, that you can ascribe it to the effect of fluidification through the addition of MgO; but if MgO is a good desulphurizer,

why should the sulphur ratio fall off after 6 or 8 pct MgO?

**Member**—The answer to the MgO is that by putting more into the basic slag you get into trouble with the basic slag itself.

**Mr. Larsen**—There is very likely a wider range of fluid slag compositions with more MgO. But the only point is in respect to the assumption involved here. We do not really know what the liquid constitution of the slag is, and I think maybe the authors might be willing to admit these are rather wild approximations.

**Dr. Grant**—They may not be exact, but they are hardly wild.

**C. L. T. Edwards** (*Dept. of Commerce, Washington, D. C. Temporarily with the Industrial Evaluation Board*)—I like everything the speakers have had to say thus far and was particularly impressed with the slight reversion as indicated in the curve.

The heat of combination between magnesium and sulphur is 2481 cal per unit weight of sulphur; the heat of combination between calcium and sulphur is 2947 cal, showing very definitely that calcium, theoretically, has a higher affinity for sulphur than magnesium does and I have found in practice, it has worked out that way in the blast furnace.

Now, in connection with manganese, iron and sulphur, I would like to tell you how, in my very small way, a few simple experiments were made in order to obtain some visible evidence concerning reactions. You scientists might do this on a more thorough scale and come up with something that is really good. Many of you, undoubtedly, have heated a mixture of powdered iron and powdered sulphur. If any of you have not done so, or seen it happen, touch the side of the crucible with a Bunsen flame and as soon as the reaction begins, remove the flame and you will find the heat will progress uniformly across the body of the mixture and, without benefit of a pyrometer, I would say the temperature of the reaction would be somewhere around 1700°F.

The heat of combination between manganese and sulphur is almost exactly double the heat of combination of iron with sulphur. Make up a mixture of manganese and sulphur in atomic proportion. Be very very careful, because the resulting reaction will be dangerous. Move the flame to the side of the crucible and be sure to have a shield for protection, as the reaction is most violent and you are lucky if everything does not fly out of the crucible. What the temperature will be, I do not know, but would guess it to be somewhere around 2700° or 2800°F.

Now, here is where the pay-off comes. Take iron sulphide, FeS, and mix it with powdered manganese; move the flame to the side of the crucible and you will find a reaction that takes place at somewhere around 1700°F. The indications are, of course, that manganese is about twice as potent a desulphurizer as iron, and it might be a good idea to keep that in mind and think about it.

I believe it to be a worthy assumption, that, since manganese sulphide has such a high melting point, there is a strong tendency for it to coagulate in the molten metal and the problem at once becomes one of mechanics, i.e., how to bring these coagulations into contact with the slag under a nonoxidizing, or reducing, atmosphere. Do not make the error of writing off manganese—learn how to use it.

## Effect of Silica Reduction on the Desulphurizing Power of Blast-Furnace Type Slags

by Nicholas J. Grant, Olaf Troili, and John Chipman

DISCUSSION, D. C. Hilty presiding

**D. C. Hilty** (*Union Carbide & Carbon Research Laboratories, Niagara Falls, N. Y.*)—How does this effect of silica compare with the effect of silica in combining with the lime in the slag to reduce the activity of CaO, thereby affecting the first equation?

**John Chipman** (authors' reply)—That is the object of showing this effect for slags of two different basicities. In the more basic, the silica is more firmly tied up in the slag and is less easily reduced. It is therefore less able to interfere with desulphurization. The important point is that silica is acting in two ways. Of course it is an acid and as an acid it ties up lime and in tying



up lime it interferes with desulphurization; but it also acts as an oxidizing agent as I have shown, and this interferes in a second way with desulphurization.

Alumina, on the other hand, although it may be an acid, does not prevent rapid desulphurization because the alumina is not reduced to any substantial extent.

In the case of MnO, we have a basic oxide which ought to supplement the other oxides in neutralizing silica or taking sulphur out of the metal, but in spite of that it interferes with desulphurization on account of its strong oxidizing power.

**D. E. Babcock** (*Republic Steel Corp., Youngstown, Ohio*)—On the first equation you have used carbon as a reducing agent and referred to the fact you did not have carbon on the open hearth. Would you not think the iron bath is a pretty powerful reducing agent with a tremendous potential?

**Dr. Chipman**—The reducing potential of the iron bath depends entirely on the oxygen content and other metals present. In the open hearth it is not a powerful reducing agent, especially at low carbon content.

**Dr. Babcock**—It is common practice to use a bessemer converter to blow out the manganese and silica, leaving the carbon almost untouched for quite a long time, indicating the carbon is not available for reaction. That is the same experience we had when we desilicized iron in the open hearth. We take out the manganese and silica, direct proportions one to the other, but do not lose the carbon, meaning the carbon in kinetic reaction is extremely slow to react. Why do we have to use carbon when it could just as well be manganese, which reacts more rapidly, or silica alone, which is more powerful and readily available to react with lime?

**Dr. Chipman**—Not necessarily. We have expressed the equations with carbon as the reducing agent since under our conditions it is the most powerful reducing agent present both in the blast furnace and in most of our experiments. The fact that silicon and manganese are removed by blowing or oreing hot metal has no bearing on the problem. The behavior of these elements is highly dependent on the slag which is entirely different in the two cases.

**Dr. Babcock**—Then are you not making the assumption

that the carbon controls the end limit and does not prescribe the mechanism, because the assumption is based on final equilibria state and not the process in between?

**Dr. Chipman**—Of course, and the equation represents, as I have said, the simplest possible way we can write the desulphurization reaction. If you wish to write it in kinetic steps (and we do not know what the steps are) the result would be most complex.

**C. E. Sims** (*Battelle Memorial Institute, Columbus, Ohio*)—We know we can get substantial desulphurization under oxidizing conditions in either the open hearth or electric furnace. Do you think the first reaction illustrates the basic reaction under this condition?

**Dr. Chipman**—This illustrates the reaction when you have carbon present. If you wish to let the "C" represent dissolved carbon, it still represents the reaction, although at a much lower carbon potential. The whole question of this reaction in intermediate slags of electric furnace type which lie between basic open hearth and blast furnace, is going to be the subject of a paper (Rocca, Grant, and Chipman) and for this reason, I would rather omit the question for the present.

**L. S. Darken** (*U. S. Steel Co., Kearny, N. J.*)—This general picture that a deoxidation, involving the removal of a relatively small amount of oxygen, is the slow step in the overall desulphurizing reaction seems to fit well the data presented. This automatically raises the question as to how we are to interpret the fact that oxygen is such a stumbling block for desulphurization, and I was wondering what Dr. Chipman would think of the possibility of blaming the slowness on the difficulty of gas nucleation?

We might think that oxygen from the MnO or the SiO<sub>2</sub> would be removed by the carbon as carbon monoxide, but if there is no gas phase in immediate contact with metal and slag, then gas bubble nucleation would be required. Does the difficulty of such nucleation fit your general picture as responsible for the slowness?

**Dr. Chipman**—I have no picture that is contrary to that. I think it is as good as any other but I had not hoped at this stage of the study to be able to identify the slow step.

## Distribution of Sulphur Between Liquid Iron and Slags of Low Iron-Oxide Concentrations

by R. Rocca, N. J. Grant, and J. Chipman

DISCUSSION, D. W. Murphy presiding

**D. E. Babcock** (*Republic Steel Corp., Youngstown, Ohio*)—With reference to eqs 7 and 8, at what temperature do they apply?

**John Chipman** (authors' reply)—That was 1600°C.

**Dr. Babcock**—You have  $1 \times 10^{-4}$  as the component for the lime and  $1$  or  $4 \times 10^{-3}$ . Now, is it by dividing one into the other you get the 400? That is assuming equivalent activity on the part of oxygen, sulphur, and magnesia.

**Dr. Chipman**—Yes, they are calculated for 1600. Now, the first one for CaO was calculated before we had a glimpse of Dr. Rosenqvist's paper.<sup>18</sup> If you take his calculation you get 14,000 cal which is very good agreement, but our calculation would be superseded by Dr. Rosenqvist's new data.

**Dr. Babcock**—The state you assume those to be in is the liquid state, as near as you can measure?

**Dr. Chipman**—Naturally it is based on the solid CaS, but if you add the effect of fusion on both sides it just about balances out, so the ratio would be about the same.

**B. M. Larsen** (*U. S. Steel Co., Kearny, N. J.*)—If we knew the activity of sulphur in the slag instead of merely the percentage, we might be able to find some

conflicting factors that balance one another out, and find that the FeO or oxygen pressure effect is really present over the whole range.

**Dr. Chipman**—I am fairly sure we would. The activity of sulphur in the slag and the activity of CaO in the slag, if we just knew those quantities, would enable us to save a lot of this computation and assumption and all the approximations we are doing now.

**Mr. Larsen**—Two other points perhaps should be included: 1—an independent effect of manganese in helping the desulphurization; and 2—the number of mols of constituents or number of mols of ions or whatever there is in the slag could vary with these compositions in such a way that you get dilution effects.

**Dr. Chipman**—You can figure all that in if you want to and it might improve the degree of approximation a little bit. Maybe enough to justify the labor of calculation, maybe not, but we did not do it.

**L. S. Darken** (*U. S. Steel Co., Kearny, N. J.*)—The authors have tackled a very complicated problem in trying to tie together in one picture the desulphurizing problem over the wide range of basicity and oxidation level from that of the open hearth to that of the blast furnace. At the present state of our knowledge of slags such an ambitious undertaking necessarily involves the adoption of numerous hypotheses.

Their formulation (eq 11) for the higher FeO range

<sup>18</sup> T. Rosenqvist: JOURNAL OF METALS (July 1951), Trans. AIME, p. 535. Discussion, this issue, p. 1047.



is similar to that presented by Darken and Larsen<sup>10</sup> except that manganese is absent in the present case. This is based on a molecular picture of slag composition, which seems less valid now but is still used because we have no adequate way of expressing the relation otherwise. The principal difference of the present treatment is the bald assumption that the distribution coefficient ( $L_{FeS}$ ) for iron sulphide varies rather markedly and gives rise to the minimum of the curves of Figs. 6 and 7. The evidence as to the nature of this variation seems rather meager, particularly as  $K'$  is apparently assumed constant;  $K'$  might reasonably be expected to vary as much as  $L_{FeS}$ , or even more, by virtue of the arbitrary nature of the calculated excess CaO. Thus the conclusions as to the effect or lack of effect of FeO (in the higher range) on the desulphurization ratio seem rather questionable. This is emphasized by the fact that the authors reach the conclusion that the sulphur combined with lime becomes negligibly small if FeO exceeds 10 pct. The efficacy of lime as a desulphurizer in this range is well attested by both mill and laboratory experience; the attribution of this effect to secondary factors seems misleading.

Since the melts of this investigation were made in a magnesia lined furnace, the slags were presumably saturated or nearly saturated with magnesia. Hence the activity of MgO is substantially constant and the contribution of MgO to the desulphurizing power of the slag would be difficult if not impossible to detect.

**Dr. Chipman**—Dr. Darken's remarks as usual are quite correct but apply mainly to the oxidizing ranges of the slag. The treatment here does not differ too much from that of Darken and Larsen.<sup>10</sup> We did not have manganese to put into the equation so that simply makes it easier. We did not know how the FeS distribution would vary with composition. We were a little afraid to assume it was constant as had been done before so we just arbitrarily said that we will suppose it is proportional to the FeO content of the slag. Certainly, we have no evidence one way or the other that this has any merit. That turns out to be a small part of the consideration in the more reducing slags with which we have been here primarily concerned. The introduction of the high FeO slag was brought into the paper mainly to show the relationship between the low FeO slags about which the paper was chiefly con-

cerned and the high FeO slags that had been studied previously. The contribution of the paper lies in the field of the low FeO slags and we claim nothing new with respect to the high FeO.

**D. J. Girardi** (*Timken Roller Bearing Co., Canton, Ohio*)—I am left with the impression that for reducing slags where FeO values are somewhere around 4 pct and under, the FeO value is much more important than the lime silica ratio; is that correct?

**Dr. Chipman**—That is correct according to our findings; perhaps not as high as 4 pct, from 2 pct on down, the FeO content is much more important than the lime.

**Dr. Girardi**—It seems as though the lime silica ratio has an insignificant effect.

**Dr. Chipman**—Not insignificant, but a small effect compared to the FeO.

**Mr. Larsen**—You do not see that some of these deviations vary much on a log scale that way. We noticed, for example, that there were large deviations in very basic high MnO slags when we tried to calculate on an excess basis concept. You tend to get ratios up to 13, 14, 15 to 1 (slag sulphur to metal sulphur) yet you cannot very well explain it on a straight excess base.

**Dr. Chipman**—How do you explain it?

**Mr. Larsen**—It fits if you consider the MnO and the free CaO as affecting the sulphur activity independently and additively. Of course, I will admit the old formula of ours was very rough.

**Dr. Chipman**—I think you have something there because MnO in the open hearth is a better desulphurizer than we have given it credit for. We have talked about MnO not being a good desulphurizer in the blast furnace slags because of oxidizing power where you do not want oxygen, but where you are already highly oxidized as in the open hearth slag-metal system, then the MnO no longer has an oxidizing power, it may be at equilibrium with Mn in the bath or substantially so. Eqs 7 and 8 show the values for  $K$  for CaO and MgO. I want to show you how MnO fits into this.

The value of  $K$  for CaO is about 400 times that for MgO. Comparing CaO with MnO the  $K$  is only twice as large. Thus MnO is a much better desulphurizer than MgO and nearly as good as CaO.

**Mr. Larsen**—Practical experience would indicate that the ratio of effect between CaO and MnO is only 2 or 3 or even less.

**Dr. Chipman**—Yes, I think it would.

<sup>10</sup> L. S. Darken and B. M. Larsen: *Trans. AIME* (1942) 150, p. 87.

## Desulphurizing Molten Iron with Calcium Carbide

by S. D. Baumer and P. M. Hulme

DISCUSSION, T. L. Joseph presiding

**B. M. Larsen** (*U. S. Steel Co., Kearny, N. J.*)—Could we have some sort of an estimate on the cost of calcium carbide for this treatment? Also, if you used calcium carbide on carbon-saturated iron, would some effect hold back the reaction?

**P. M. Hulme** (authors' reply)—As far as I know we have not worked on carbon-saturated iron. About 3½ pct C is the highest we have worked on. As far as cost goes, it depends on how much sulphur you have to take out. It will run anywhere from \$0.75 to \$2.00 a ton overall cost including the cost of carbide per ton of metal treated. That is, using the efficiencies that we show in this paper. We are getting better efficiencies now.

**T. L. Joseph** (*University of Minnesota, Minneapolis, Minn.*)—Did you say 2 lb of calcium compound?

**Mr. Hulme**—That is based on 10 lb of calcium carbide per lb of sulphur removed.

**D. E. Babcock** (*Republic Steel Corp., Youngstown, Ohio*)—We have run this type of desulphurization process at the blast furnace. We have desulphurized between 100 and 200 at the blast furnace and taken the

iron right out of the furnace with an injector system. The process gave us quite varied results; stratified iron, high sulphur on the top and low sulphur on the bottom, and we decided it was impractical.

**Mr. Hulme**—Just what was the type of injection equipment?

**Dr. Babcock**—Nitrogen gas for one injection method and we used fairly large gun equipment. We followed the same general type of pattern you show only on a larger scale.

**Mr. Hulme**—It sounds very much like what we call the gale of wind method. We have very erratic results with that.

**Dr. Babcock**—We have tried several types, and particle sizes. The operation was not satisfactory.

**Mr. Hulme**—Of course, we have never tried it on that scale except on a continuous basis. That is the reason we abandoned the idea of working on 35 ton ladles on a batch principle and took it as it came out of the cupola and treated it on the fly on a continuous basis.

**Dr. Babcock**—When you compare the relative effectiveness of the process as carried out, it does not give a very favorable comparison of that process which is already developed. We did not feel it was worth the

money and effort to go any further, since it did not show the performance and simplicity of the other process.

**Mr. Hulme**—I am a little doubtful of its value on the blast furnace scale. It seems to have possibilities in the foundry.

**Dr. Babcock**—That may be true.

**John Chipman** (*Massachusetts Institute of Technology, Cambridge, Mass.*)—There is one question I would like to ask; it has to do with the use of calcium carbide and calcium oxide together in the desulphurization. As I recall, the efficiency of calcium carbide as

a desulphurizer was considerably damaged by the presence of calcium oxide. This suggests the possibility that something is going in with calcium oxide, perhaps calcium carbonate or calcium hydroxide or some other impurity of an oxidizing nature. If that is so, perhaps it should be repeated, using dead burned lime along with the calcium carbide.

**Mr. Hulme**—It was burnt lime and probably had some hydroxide in it.

**Dr. Chipman**—It might be quite different with freshly burned lime then.

**Mr. Hulme**—You are right.

## Desulphurization of Pig Iron with Pulverized Lime

by Bo Kalling, C. Danielsson, and Ottar Dragge

and

## Kalling-Domnarfvet Process at Surahammar Works

by Sven Fornander

### DISCUSSION, T. L. Joseph presiding

**L. F. Reinartz** (*Armco Steel Corp., Middletown, Ohio*)—I would like to know, in the practical application of the Kalling process, what kind of a lining was used, how thick was the lining, and how much metal was treated at one time?

**S. Fornander** (author's reply)—The rotary furnace is lined with a course of fireclay bricks 6 in. thick. This course is backed by 5 in. of insulation. The furnace has a capacity of about 15 tons.

**Mr. Reinartz**—How was the ladle preheated?

**Mr. Fornander**—As pointed out in the paper, the furnace was heated by a gas flame in the beginning of the experiments. During these first tests, however, the desulphurization was inconsistent. We think that this was due to the fact that iron droplets sticking to the furnace walls were oxidized by the gas flame. Now, the furnace is operated without preheating of any kind, and the results are much better.

**T. L. Joseph** (*University of Minnesota, Minneapolis, Minn.*)—I might add one comment. This furnace was heated with a flame and for a time they had a little difficulty due to some residual metal in the rotating drum that would oxidize in between treatments and they found therefore, that it was very essential to drain the drum completely of metal so that they would not build up any ferrous oxide between treatments and they eliminated some of their erratic heats by maintaining those more reducing conditions.

It was interesting to watch this operation. As soon as the drum started to rotate there was considerable flame, at least, at the time I saw it, that came out around the flanges, indicating there was quite a little pressure on the inside of the drum.

**W. O. Philbrook** (*Carnegie Institute of Technology, Pittsburgh*)—Is the reaction slag in the Kalling process liquid or solid, and how is it separated from the metal?

**Mr. Fornander**—In the process there is no slag in the usual sense of the word. The lime powder does not melt during the treatment. After the treatment the lime is still in the form of a fine powder. It is separated from the metal by means of a piece of wood of suitable size placed within the furnace before it is emptied.

**D. C. Hilty** (*Union Carbide & Carbon Research Laboratories, Niagara Falls, N. Y.*)—Dr. Chipman has given us some of his ideas in connection with a specific effect of silicon and silica on sulphur elimination and how silicon might interfere with desulphurization

in the blast furnace. I wonder if he would like to elaborate on the possibility of a similar effect of silicon in the Kalling process?

**J. Chipman** (*Massachusetts Institute of Technology, Cambridge, Mass.*)—Silicon does not interfere with the Kalling process. Anything that has strong reducing action is good for desulphurization. In these tests where the temperature was low compared to blast furnace temperatures, the silicon that is in the metal is a better reducing agent than the carbon. At high temperatures, carbon is the better. It is not the silicon in the metal that interferes with desulphurization, it is the silica in the slag.

**Mr. Joseph**—I might add that the metal that was tapped from the drum after desulphurization was really at quite a low temperature. It was not measured, but I think it was well under 1300°C, probably 1200° or a little above that. That was one of the difficulties, and I think there is no question about the fact that the Kalling process—in that it affects desulphurization between powdered lime, solid and liquid iron—is a reaction definitely between the solid lime and the liquid iron.

**E. Spire** (*Canadian Liquid Air, Montreal, Canada*)—This Kalling process seems very interesting to us and after all it is only a mixing action that is taking place between the iron and the slag. We have attempted to do the same thing in another way. We have placed at the bottom of the ladle a porous plug through which we injected an inert gas. It can be nitrogen or argon. This plug is placed at the bottom of the conventional ladle and gas injected through the plug. That has appeared in our patent.

To define this new type of treatment, I use the word gasometallurgy. I do not know if you like it, but it is a way of defining methods of treating metal using gases. What we do is exactly what is done in the exchange process in another way. We have a porous plug at the bottom with a high lime slag on top of the metal. Using this method, we have very good agitation of metal and slag, and with a small flow of gas, we can achieve a very strong agitation. For instance, in the 500 lb ladle, we use only 5 liters of gas a minute. We have an agitation compared to very rapidly boiling water in a pail. Moreover, the agitation can be controlled to create any amount of mixing desired.

In a few minutes, with this method, the sulphur dropped from 0.58 to 0.11. These results have been improved since, and we have obtained results like 0.08



to 0.015 in a matter of 10 min, but what is interesting is that we have been able to do that in steel, too.

In steel, we have done exactly the same thing with a high lime slag containing a certain amount of carbon. We have obtained a reduction of 0.5 to 0.25 or, recently, from 0.5 to 0.020. This is interesting because it was done in only 3½ min, and these results, I think, are worth-while because it could be very well used with furnaces where no desulphurization can take place.

All of this work has been done with the help of the Canadian Government and the Bureau of Mines, Ottawa, (now, the Department of Mines and Technical Surveys). I just wanted to point out this new process as having good possibilities in the iron and steel industry where the sulphur problem is such a big one.

**Mr. Joseph**—Will you tell us about the gas that goes in and the slag that is formed?

**Mr. Spire**—The gas we are using is either argon or nitrogen. In the case of iron, nitrogen works well. In the case of steel, we started by using nitrogen. This gave us trouble with blowholes in the steel. Using argon, we had perfectly sound ingots. The flow was 5 liters a min and with that we had a strong agitation. We found no difference if the ladle was full or half empty as far as agitation was concerned, and we expect in large-scale developments, which will take place very soon, that the flow of gas will not be very much greater.

For iron, we have to use a fairly liquid slag and we have been trying lime and soda ash. We have been trying sodium carbonate and calcium carbonate and that was probably the best we have used. It worked very well. The weight was around 2 pct. For steel, we have been using various slags. We are planning to use some Perrin slags. The agitation we obtained is similar to the Perrin process, only we have a longer time for reaction taking place. The Perrin slag is a very good slag in connection with that. We have also been using a simple lime mixture with a certain amount of carbon in order to reduce the FeO content to a minimum.

**Mr. Larsen**—Do you have to have the gas flow on all the time that the metal is in contact with the porous refractor?

**Mr. Spire**—We prefer to have the gas going on all the time for various reasons. I may say that the refractory problem is not very simple. The way the porous plug is fixed to the bottom gave us trouble for several months, and I think we have straightened out this problem and the porous refractory can be used. We have used the same one for 30 heats in the 500 lb ladle. We do not have any more difficulty, but now we expect to run larger heats to see what we will get.

**C. H. Bacon** (*John Summers & Sons, Ltd., Shotton, Chester, England*)—What type of refractory is being used for the porous plug for the steel ladle?

**Mr. Spire**—We have been using brucite-type magnesium oxide.

## Solution Loss and Reducing Power of Blast Furnace Gas

by T. L. Joseph

DISCUSSION, A. H. Sommer presiding

**S. T. Killian** (*Johnstown, Pa.*)—This is one of the finest papers I have read. Tying in stoichiometric calculations with furnace performance and practice is a step which had to be taken sooner or later. The noteworthy difference between Dr. Joseph's type of calculations and regular blast furnace calculations is that the lb mol system is used as a basis. With the lb mol system, weights, volumes, and chemical reactions can all be expressed in the same equation.

In the paper, wind, ore, flux, and fuel are all expressed as lb or lb mols. Probably Dr. Joseph does not realize it, but the vague word coke appears only twice in the entire paper. Lb of C and lb mols of C are followed through reactions but the word coke appears only as 1560 lb coke per ton of pig and 1700 lb of coke per ton of iron. Obviously in order to understand furnace reactions, the coke should be expressed as lb or lb mols of C. Furnaces can also be compared more easily.

In some respects the paper is too thorough and too complete. The effects of the metalloids reduced into the iron upon the top gases represents a difference of less than 3 pct of the CO formed in the bosh. Due to the completeness of the calculations in relation to the CO/CO<sub>2</sub> ratio, this was included and was necessary. However, the exclusion might have enabled more furnace men to follow the lb mol system of calculations through the blast furnace to a better degree. By considering only irons of similar analysis, this part of the calculations might have been omitted. However, if this had been done, total rewriting of the paper later would have been necessary in order to make the work complete as it is now. It also would not have been nearly as authoritative.

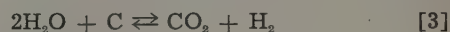
In the paper, there appears the reaction:



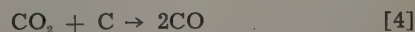
Dr. Joseph states that he did not take this reaction into

consideration in any calculations pertaining directly to the paper. The probable reason for this is that although it contains all the main reacting top gases except N<sub>2</sub>, it is rather inflexible since it is monomolecular in relation to each of the reacting gases and does not tie in with the gasification of C.

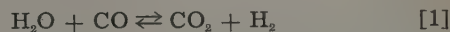
Actually the reactions:



and the solution loss reaction:



tend to assume an equilibrium through the reaction:



which should be considered a balancing or equilibrium reaction. Reactions 2, 3 and 4 permit furnace conditions to balance with the CO/CO<sub>2</sub> ratio and H<sub>2</sub> formation. They tie in with the solution loss. Reaction 1 unites them chemically.

Probably the best calculation to make at this time would be to try to find the relative importance of the CO<sub>2</sub> from the flux and the H<sub>2</sub> in the dilution on an actual furnace gas analysis. For this purpose the Dobbscha-Carnegie-Illinois paper—"Effect of Sized and Sintered Mesabi Iron Ores On Blast Furnace Performance" is chosen. This paper was presented before the blast furnace section of the AIME in 1948. This represents the best large scale furnace operation available to me. Unfortunately the changes were brought about by beneficiation of the burden and not by changes on one burden.

In choosing the basis for the calculation in relation to the furnace, 100 mols of dry top gas is chosen. This leaves something to be desired inasmuch as the nitrogen basis is changing but I believe it will be better understood than any other type and it is the easiest to use.

The gas analysis and mols per 100 mol of blast furnace gas of the furnaces compared are:

|                 | Normal Ores |        | Prepared Ores |        |
|-----------------|-------------|--------|---------------|--------|
|                 | Pct         | Mol    | Pct           | Mol    |
| CO              | 26.57       | 26.57  | 26.17         | 26.17  |
| CO <sub>2</sub> | 12.33       | 12.33  | 12.40         | 12.40  |
| H <sub>2</sub>  | 2.30        | 2.30   | 1.60          | 1.60   |
| CH <sub>4</sub> | 0.13        | 0.13   | 0.13          | 0.13   |
| N <sub>2</sub>  | 58.67       | 58.67  | 59.70         | 59.70  |
| Total           | 100.00      | 100.00 | 100.00        | 100.00 |

Relative Amounts of CO<sub>2</sub> Evolved from Flux

In the paper, the distribution of the lb C per ton of iron in the top gases was given as follows:

|                       | Normal Ores | Prepared Ores |
|-----------------------|-------------|---------------|
|                       |             |               |
| CO                    | 1024        | 838           |
| Total CO <sub>2</sub> | 475         | 397           |
| Flux CO <sub>2</sub>  | 113         | 76            |

Since the amount of flux CO<sub>2</sub> in the total CO<sub>2</sub> is given, the flux CO<sub>2</sub> in the gas can be calculated directly:

|                                      | Normal Ores     | Prepared Ores  |
|--------------------------------------|-----------------|----------------|
|                                      |                 |                |
| Mol CO <sub>2</sub> in gas from flux | 113/475 x 12.33 | 76/397 x 12.40 |
| Mol CO <sub>2</sub> in gas from flux | 2.93 mol        | 2.37 mol       |

Relative Amounts of H<sub>2</sub> Formed

"Making, Shaping and Treating of Steel" by Camp and Francis contains the following notations on the blast furnace diagram:

- 875°C—much of the carbon dioxide is reduced by carbon
- 975°C—Combined water remaining is decomposed
- 1075°C—limestone is decomposed.

The evolution of CO<sub>2</sub>, the driving off of combined water, the H<sub>2</sub> formation, and the solution loss are tied in so closely that it may be impossible to separate them absolutely, but a start should be made. Probably the best way to correlate the H<sub>2</sub> formation from the efficient to the normal furnace would be through an H<sub>2</sub> to flux CO<sub>2</sub> ratio, since the normal furnace would eliminate the cooling and combined water farther down in the furnace with a consequential greater H<sub>2</sub> formation and a greater solution loss.

|                                                | Normal    | Prepared  |
|------------------------------------------------|-----------|-----------|
| Mol H <sub>2</sub> to mol flux CO <sub>2</sub> | 2.30/2.93 | 1.60/2.37 |
| Ratio                                          | 0.785     | 0.675     |

Thus if the furnace using normal ores decomposed as little water as the efficient furnace, the normal top gas would contain:

2.93 x 0.675 = 1.98 mol H<sub>2</sub>

This would leave:

2.30 - 1.98 = 0.32 mol H<sub>2</sub>

as excess H<sub>2</sub> decomposed in the normal furnace. Thus the 0.32 mol of H<sub>2</sub> would not have been formed if the normal furnace had worked as well as the efficient furnace. This excess can not be considered as being independent of the solution loss because it is probably tied in very closely with it. However it does represent excess H<sub>2</sub> in the gas and is so considered.

A breakdown of the calculations shows:

|                                  | Normal Ores |        | Prepared Ores |        |
|----------------------------------|-------------|--------|---------------|--------|
|                                  | Mol         | Pct    | Mol           | Pct    |
| CO                               | 26.57       | 26.57  | 26.17         | 26.17  |
| Combustion CO <sub>2</sub>       | 9.40        | 9.40   | 10.03         | 10.03  |
| Flux CO <sub>2</sub> (efficient) | 2.37        | 2.37   | 2.37          | 2.37   |
| Flux CO <sub>2</sub> (excess)    | 0.56        | 0.56   | 0.00          | 0.00   |
| H <sub>2</sub> (efficient)       | 1.98        | 1.98   | 1.60          | 1.60   |
| H <sub>2</sub> (excess)          | 0.32        | 0.32   | 0.00          | 0.00   |
| CH <sub>4</sub>                  | 0.13        | 0.13   | 0.13          | 0.13   |
| N <sub>2</sub>                   | 58.67       | 58.67  | 57.90         | 57.90  |
| Total                            | 100.00      | 100.00 | 100.00        | 100.00 |

In the above table based upon 100 mols of blast furnace gas and comparing the furnace using normal ores with the furnace when using prepared ores, we find 0.56 mol additional due to excess flux CO<sub>2</sub>, 0.32 mol additional due to excess water decomposition, and the remainder (with the type of calculations used) of 0.15 mol to be attributed directly to the solution loss reaction with no side reactions. However the solution loss reaction is tied in with the other reactions so closely that nearly 100 pct of the change must be considered as stemming from the carbon going into solution and the resulting interaction with H<sub>2</sub>O in the gaseous phase.

The figures seem to show that while the solution loss itself is masked by side reactions, the dilution of the N<sub>2</sub> is not diminished by them but is augmented by the resulting H<sub>2</sub> formation. Basically the principle of N<sub>2</sub> dilution due to the solution loss seems to work out better with the resulting additional water decomposed.

Attention is again called to the fact that the figures used do not represent a change in solution loss with no change in the burden. They represent a change from a burden of normal ores on a normal furnace to a burden of beneficiated ores being reduced more efficiently on the same furnace.

I regret that I can add nothing of value to Dr. Joseph's paper. By all standards it must be accepted as one of the finest papers produced.

Oxygen in Liquid Open-Hearth Steel—Oxidation during Tapping and Ladle Filling

by T. E. Brower, J. W. Bain, and B. M. Larsen

DISCUSSION, R. C. Solomon presiding

John Chipman (Massachusetts Institute of Technology, Cambridge, Mass.)—In tapping a heat of steel from the open hearth it is difficult, as the authors have pointed out, to distinguish between oxidation by air and oxidation by reaction with the slag. These effects could be distinguished and the oxidation due to air more closely identified if the same method were applied to tapping electric furnaces. Here the slag can be made reducing and the bath presumably uniform, thus changes due to air oxidation from furnace to ladle should be capable of more exact determination.

It should be pointed out also that if the amount of oxygen picked up from the air is as great as the authors have indicated, there is little incentive to produce an entirely deoxidized bath in the electric furnace. The use of a reducing slag for controlling alloy elements and for desulphurization is understandable. But from the standpoint of deoxidation its effect would be entirely lost in tapping if the reaction with air is comparable with that reported here. C. H. Bacon (John Summers & Sons Ltd., Shotton, Chester, England)—I was particularly interested to see the films of the tapping streams, as we have taken some high speed films of the teeming streams between



the ladle and the mold. The original purpose of taking the films was not connected with oxidation, but we found that the form of the metal streams varied greatly; some of the streams were relatively compact, whereas others were very ragged. I should like to ask Mr. Larsen for his views on the degree of oxidation that takes place between the ladle and the mold, and to what extent this might be influenced by the form of the stream.

**N. R. Arant** (*Titanium Alloy Manufacturing Co., Pittsburgh*)—The results and motion picture studies in this paper indicate that perhaps a great deal can be learned if the oxidizing and nitrifying effect of air during tapping is accentuated. One way to observe this effect would be to consider the elements which more readily react with air, namely; aluminum, titanium, and zirconium. Since steels containing both titanium and aluminum are in widespread production, these would be the ones to test. The more common grades produced in the arc-electric furnaces are: 321 (18-8 Ti), 17 pct Cr-Ti, 5 pct Cr-Mo-Ti and 19-9DL.

Both titanium and aluminum have a strong affinity for nitrogen as well as oxygen; therefore, if the steels mentioned above can be tapped with a minimum of contact with air, a much cleaner final product might result, with fewer titanium nitride and aluminum oxide nonmetallic inclusions. Furthermore, since ferro titanium and aluminum are expensive, there is the possibility of a considerable saving in the cost of producing the ingots.

In comparing standard tapping methods with the tilted-ladle method while considering the active elements mentioned above, it may be possible to more accurately calculate the volume of air which comes in contact with the steel during tapping.

To obtain accurate data during tapping, I believe it is necessary to obtain representative samples of metal and slag before tap, from the ladle, and during teeming. If good samples are used it seems logical that a clearer picture can be obtained regarding the oxidizing and nitrifying of alloying elements during tapping and ladle filling.

**R. K. Kulp** (*Electro Metallurgical Co., Division of Union Carbide & Carbon Corp., Pittsburgh*)—Metallurgists have made frequent reference to the problems involved in determining the reactions which occur during the tapping of open hearth heats. The authors of this paper are to be commended for developing the "air oxidation" method of determining the amount of reaction taking place during tapping and ladle filling.

This paper was presented before at the 1950 Open Hearth Conference, and at that time a discussion was presented by Mr. Tenenbaum. He offered data which indicated that the degree of air oxidation was less on heats which were blocked than on heats which were tapped open. In his rebuttal, Brower failed to agree with Tenenbaum's statement that "losses of elements dissolved in steel prior to tap are generally small." Do the authors have any specific information on air oxidation of blocked vs. open heats which would indicate a difference due to initial deoxidation?

**B. M. Larsen** (authors' reply)—Dr. Chipman's idea of separating slag and air oxidation by using data from electric furnace heats with reducing slags at tap is a logical one. We have obtained data on a few such heats but the method of estimating oxidation by difference, from alloy materials balances, gave inconclusive results. Both the quiet metal bath and the tap stream tend in this practice to be quite inhomogeneous and the sampling problem is an almost impossible one. Thus we feel that such evidence is not nearly as good as that given in the paper, which indicates a relatively negligible effect from reaction with slag. These data on electric steel heats did indicate a large loss by air oxidation, and in spite of the uncertainty caused by variable analyses and the difficulties of representative sampling, we believe that much of this oxidation loss is real, and that with respect to the final ingot, at least, deoxidation is essentially dependent, not on the

reducing slag, but on the deoxidizing alloys just as it is in the open hearth. Thus, the tendency for much electric steel to be cleaner than open hearth remains about as much of a mystery as ever from any data we have obtained to date.

We did try to obtain the "representative samples" listed by Mr. Arant. However, the sampling here is a problem at best. Fortunately, the metal in open hearth baths is usually well mixed on heats tapped open. Blocked heats show somewhat more variability in tap stream composition.

We cannot give a definite answer to Mr. Bacon's question about oxidation between ladle and mold, although a few inconclusive indications from inclusion counting vs. various controlled and uncontrolled teeming conditions did indicate the probable existence of a relatively smaller effect which we rather believe did tend to increase inclusion content in the ingot. As noted in our comments on "oxidation effects and steel quality" in the paper, we suspect that certain factors are present which are perhaps not yet even recognized or at least are poorly understood. At least it appears that ragged or spraying teeming streams are worth taking some pains to avoid.

For a really conclusive answer to Mr. Kulp's question about relative alloy losses between blocked and open heats, comparative data on groups of 20 to 30 or more heats in the same grades of steel should be used. The pattern of variability in tapping conditions is so haphazard that results on smaller groups are not very reliable unless the factors involved have a large effect. However, the following data are on three small groups of killed heats, all of them medium to high carbon, mostly around 0.50 to 0.60 pct C at the platform:

|                                | No Block,<br>Tapped on<br>Carbometer—<br>Fine Grain | Blocked Heats   |                   |
|--------------------------------|-----------------------------------------------------|-----------------|-------------------|
|                                |                                                     | Fine<br>Grained | Coarse<br>Grained |
| No. of heats averaged in group | 7                                                   | 8               | 10                |
| Loss, lb per ton, Mn           | 1.67                                                | 1.85            | 1.19              |
| Loss, lb per ton, C            | 0.30                                                | 0.66            | 0.50              |
| Loss, lb per ton, Si           | 0.80                                                | 0.66            | 0.97              |
| Loss, lb per ton, Al           | 0.85                                                | 0.68            | 0.45              |
| Total alloy loss, lb per ton   | 3.62                                                | 3.85            | 3.11              |
| Lb oxygen per ton, external    | 2.58                                                | 2.55            | 2.38              |

Differences here are small, especially in terms of the indicated weight of oxygen reacting (from sources outside of the metal, presumably from air). The coarse grained heats had less aluminum loss, which is reasonable, and less manganese loss most likely because the oxygen happened to react more with the silicon. In total alloy losses, one group of blocked heats was higher, the other lower, than the heats tapped open with no furnace block. As shown by Brower in an earlier discussion<sup>6</sup> of this same paper that although aluminum and silicon and perhaps manganese (when high in fines) probably are all lost to some extent by floating and burning at the surface (aluminum may also react to some appreciable extent with ladle lining surfaces), yet quite large losses can occur from alloys definitely dissolved in the iron solution by some external effect which, directly or indirectly, would seem to be from atmospheric oxygen. Such an effect, almost obviously, is independent of any blocking or other occurrence in the furnace before tap.

As a purely practical matter, blocked heats with much of the alloy additions made in the furnace before tap probably do have somewhat lower average losses after tap, but the added losses in the bath before tap are such that total alloy loss is generally equal to or greater than in heats tapped open. That blocking improves quality is at least very doubtful, and it is certainly wasteful of alloys and of furnace time. Though sometimes needed for other practical reasons, in the writer's opinion, the blocking of heats should be avoided as much as possible.

<sup>6</sup> Open Hearth Proceedings, AIME (1950) 33, pp. 180-183.

# Discussion — Institute of Metals Division\*

St. Louis Meeting, February 1951

|                                                                                                                                                                                                   |      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
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| Crystal Structures and Transformations in Indium-Thallium Solid Solutions (paper by L. Guttman. JOURNAL OF METALS, December 1950, p. 1472).....                                                   | 1056 |
| Crystallography of Cubic-Tetragonal Transformation in the Indium-Thallium System (paper by J. S. Bowles, C. S. Barrett, and L. Guttman. JOURNAL OF METALS, December 1950, p. 1478).....           | 1057 |
| Grain Growth and Recrystallization Characteristics of Zirconium (paper by F. J. Dunkerley, F. Pledger, V. Damiano, and J. Fulton. Discussion published with the paper, this issue, p. 1003).      |      |
| Interface and Marker Movements in Diffusion in Solid Solutions of Metals (paper by L. C. Correa da Silva and R. F. Mehl. JOURNAL OF METALS, February 1951, p. 155) .....                          | 1060 |
| Torsion Texture of Copper (paper by W. A. Backofen. JOURNAL OF METALS, December 1950, p. 1454).....                                                                                               | 1062 |
| Effect of Ferrite Grain Structure Upon Impact Properties of 0.80 Pct Carbon Spheroidite (paper by M. Baeyertz, W. F. Craig, Jr., and E. S. Bumps. JOURNAL OF METALS, December 1950, p. 1465)..... | 1064 |
| Effect of Alloying Elements on True-Stress True-Strain Flow Curves of Pearlitic Steel (paper by R. Raring, J. A. Rinebolt, and W. J. Harris, Jr. JOURNAL OF METALS, May 1951, p. 395).....        | 1065 |
| Transitions in Chromium (paper by M. E. Fine, E. S. Greiner, and W. C. Ellis. JOURNAL OF METALS, January 1951, p. 56).....                                                                        | 1066 |
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| Graphite-Rod Hairpin-Resistor Radiation Furnace for High Temperatures (paper by W. J. Kroll, W. W. Stephens, and J. P. Walsted. JOURNAL OF METALS, November 1950, p. 1394).....                   | 1074 |
| Ignition Temperatures of Magnesium and Magnesium Alloys (paper by W. M. Fassell, Jr., L. B. Gulbransen, J. R. Lewis, and J. H. Hamilton. JOURNAL OF METALS, July 1951, p. 522).....               | 1075 |
| Mechanical Properties of Stainless Steel Powder (paper by A. H. Grobe and G. A. Roberts. JOURNAL OF METALS, February 1951, p. 125).....                                                           | 1076 |
| Rate of Sintering of Copper Under a Dead Load (paper by F. N. Rhines and H. S. Cannon. JOURNAL OF METALS, July 1951, p. 529).....                                                                 | 1076 |

\* TP 3174E. Since some of the annual meeting papers had not been published sufficiently in advance of the time this discussion went to press, discussion of these papers will appear when discussion is published in the spring.

## Metallographic Study of the Martensite Transformation in Lithium

by J. S. Bowles

DISCUSSION, M. Cohen presiding

**J. W. Christian** (*The Inorganic Chemistry Laboratory, Oxford, England*)—I was very interested in Dr. Bowles' results on the suppression of the transformation by solid films of alcohol or propane. The transformation in cobalt, which is also martensitic, can be explained by a mechanism involving the reflection of "half dislocations" down a series of atomic planes.<sup>12</sup> This reflection process is similar to that considered by Frank<sup>13</sup> for plastic deformation on a single slip plane and, as he pointed out, reflection would be impossible if the metal were immersed in a liquid of higher density. It seems possible that solid films of alcohol have a similar effect on the lithium transformation.

Reflection should also be possible at a grain boundary, though a higher kinetic energy of the dislocation, and hence a lower temperature would be required. As Dr. Bowles used coarse grained polycrystalline speci-

mens, transformation on cooling should still have occurred in grains which did not form part of the outside (free surface) of the metal. This may account for the X-ray lines of the low temperature phase which were found. There is thus the interesting possibility that in a polycrystalline specimen a liquid, or in some cases a solid, film of material of comparable or higher density will lower  $M_s$ , while in a single crystal it should suppress the transformation completely.

In the case of cobalt it is necessary to find a dense liquid which will not react with the metal at the transformation temperature. The most promising liquid appears to be pure lead, but it is very difficult to devise a method of investigating whether or not this does suppress the transformation.

<sup>12</sup> J. W. Christian: *Proc. Royal Soc.* (1951). In course of publication.

<sup>13</sup> F. C. Frank: Report of Bristol Conference on the Strength of Solids, p. 57. The Physical Society, London.

## Crystal Structures and Transformations in Indium-Thallium Solid Solutions

by Lester Guttman

DISCUSSION, M. Cohen presiding

**A. H. Geisler and D. L. Martin** (*General Electric Research Laboratory, Schenectady, N. Y.*)—We were rather interested to note the author's conclusion that

the cubic to tetragonal transformation may be of the second order, for we have been able to show that the order-disorder transformation in an analogous alloy system is a first-order transformation with a discon-



tinuous change in composition, rather than the frequently assumed second-order type.<sup>14</sup> Although it seems questionable whether the heterogeneous equilibrium of a martensitic reaction may be described, the author has attempted to define the reaction type, and on this basis we should like to examine the evidence further. In our work we have stressed the importance of establishing equilibrium, which may require hundreds of hours at relatively high temperatures. It is our contention that lack of equilibrium leads to results that suggest the so-called second-order type of transition. Here the author has attempted to attain equilibrium in time intervals of slightly more than a few minutes. We would like to know whether the transformation was studied using any appreciable annealing periods in those cases in which two-phase structures were merely assumed to be nonequilibrium.

In regard to the supposed continuity of volume shown by Fig. 3, if the curve were drawn through the data points for the 12½ and 18 pct alloys, there would be a discontinuity between 18 and 19 pct Tl. This would suggest a first-order transformation with a two-phase field at these compositions and the specified annealing temperatures of 105° to 135°C. These conditions agree with the boundary in the phase diagram, Fig. 9, but require that there should be two boundaries. On the other hand, the data in Table I appear to apply to the structure at room temperature and if this is so, it seems inconsistent to assign any special merit to the data plotted by full circles which are specified as "more thoroughly annealed specimens" where the annealing refers to 105° to 135°C and not room temperature. Thus it is questionable whether these data could support a conclusion regarding the type of reaction.

The author has observed that the data indicate no two-phase region wider than about 0.5 pct Tl at room temperature. This hardly seems an adequate basis for concluding that the cubic-tetragonal transformation is one of the second order rather than of the first order. We are sure that the author considers the liquid to solid transformation in the indium-rich alloys as the first-order type, yet the phase diagram, Fig. 9, fails to show width in the liquid plus solid field for alloys up to 30 pct Tl. Naturally, the minimum accounts for zero width at one point only. In fact there are many binary systems in which the two-phase field between a liquid and solid solution is very narrow or has escaped detection. Similarly the fields between two solid phases such as ferrite plus austenite in most of the  $\gamma$  loop forming systems of the iron-rich alloys are narrow. The A.S.M. Handbook shows a 0.1 pct maximum range for Fe-V. The two-phase fields between the ordered and disordered phases in Co-Pt alloys with 18 to 26 pct Co are less than 0.5 pct Co in width but still are detectable. In this case we found that electrical resistance measurements were most convenient for determining boundaries of the two-phase fields.

Since the two-phase region, if it exists between cubic and tetragonal phases in In-Tl alloys, is narrow, additional evidence is needed before the type of transformation can be definitely established. Perhaps, as the author noted, highly precise measurements of the heat capacity are needed to distinguish a first from a second-

order transformation, but there may be some doubt that the sensitivity of thermal methods is as good as that of currently used techniques. Apparently the only practical deciding test for a two-component system is whether or not there is an "unambiguous" two-phase region. The test has not yet yielded conclusive results for many systems including the order-disorder reaction in  $\beta$  brass.

**L. Guttman** (author's reply)—The comments of Drs. Geisler and Martin are valuable for drawing attention to portions of the paper which are obscure, partly for reasons of language. It is hoped that the following formulation will clarify the basis for my conclusions, which remain essentially unchanged.

The evidence summarized in Table II is that the cubic-tetragonal transformation, both on heating and cooling, is complete in a temperature interval of less than 10° centered on the line drawn in Fig. 9. Hence the equilibrium boundary or boundaries must lie within this region, which is about 0.5 atomic pct wide at all temperatures, the slope of the line being roughly 20° per atomic pct Tl.

The effect of uniform long annealing is to decrease the fluctuations of a few hundredths of 1 pct in the lattice parameters apparently caused by severe deformation, which would otherwise obscure the changes associated with the transformation itself. The choice of the phrase "approach to equilibrium" to describe this process of stress relief was unfortunate. However, aside from the uncertainties due to this effect and to the hysteresis between the direct and reverse transformations, the question to be decided from Fig. 3 is whether there is any discontinuity in volume in the vicinity of 22.7 pct Tl, where the structure changes from tetragonal to cubic at room temperature; the annealing temperature itself is immaterial as long as it is high enough; since the high temperature structures cannot be undercooled more than a few degrees, see also Fig. 8.

Shortly after the present work was submitted, there appeared a similar study by Makarov<sup>15</sup> which agrees in finding no two-phase region between the cubic and tetragonal forms, and places the boundary at about 25 pct Tl at room temperature.

The relevance to the present case of arguments based on other systems is of course questionable; moreover, they should not be allowed to confuse the generally valid criterion that the absence of a two-phase region means that the transformation is of higher order than the first, and vice versa. In particular, examination of the data of Valentiner,<sup>2</sup> which could not be adequately shown in Fig. 9, will reveal definite separation of liquidus and solidus between 0 and 12 pct Tl, even in this very unfavorable case of a minimum melting point only 4° below that of pure In.

Finally, the intention of the comment in the footnote (p. 1477 of the paper) was obviously not to recommend thermal methods for characterization of transformation order in solids.

<sup>14</sup> J. B. Newkirk, R. Smoluchowski, A. H. Geisler, and D. L. Martin: *Journal of Applied Physics* (April 1951).

<sup>15</sup> E. S. Makarov: *Izvest. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk.* (1950) pp. 485-491.

## Crystallography of Cubic-Tetragonal Transformation in the Indium-Thallium System

by J. S. Bowles, C. S. Barrett, and L. Guttman

DISCUSSION, M. Cohen presiding

**A. H. Geisler and D. L. Martin** (*General Electric Research Laboratory, Schenectady, N. Y.*)—The authors have very nicely demonstrated that the observed data

agree much better with a proposed double-shear mechanism than they do with an assumed twinning mechanism. Reference is made to our results on an analogous alloy, Co-Pt in which a disordered cubic phase transforms to an ordered tetragonal phase.<sup>14</sup> True, our con-



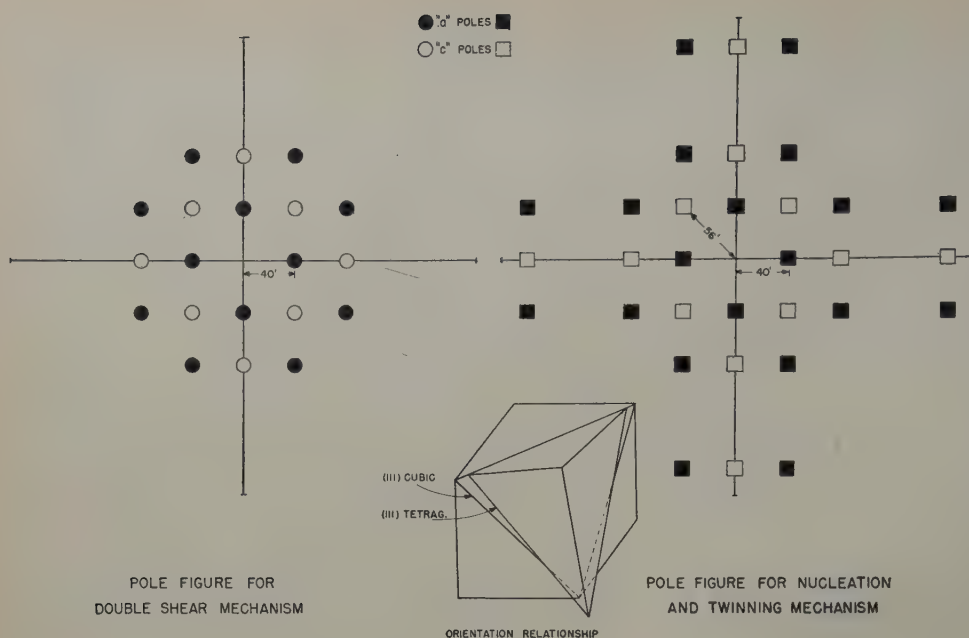


Fig. 14—Array of poles for tetragonal structure formed by transformation mechanism proposed by the authors (left) and that for nucleation and growth on  $\{111\}$  planes with first generation twinning (right).

clusion that the tetragonal lattice has the same orientation as the cubic lattice is only an approximation. Actually coherent platelets on  $\{110\}$  planes require that some of the tetragonal axes make angles of  $27'$  to  $43'$  (depending on  $c/a$  ratio) with cube axes according to the orientation relationship  $(110)_D // (101)_O$  and  $[001]_D // [010]_O$ .

We should like to suggest that a better assumption might be made for evaluating the twinning mechanism in In-Tl alloys rather than assuming that the original

cubic crystal becomes tetragonal by simple expansion along one cube axis and contraction along the other two, without change of orientation. In this case coherency on  $\{111\}$  planes appears to be promising. That is, a probable mechanism to test the twinning hypothesis would be to assume that the tetragonal phase formed from the cubic phase by growth of platelets on  $\{111\}$  planes with the tetragonal lattice being attained by adjustments in the spacing and atomic positions of  $\{111\}$  cubic planes. It is interesting to note that this

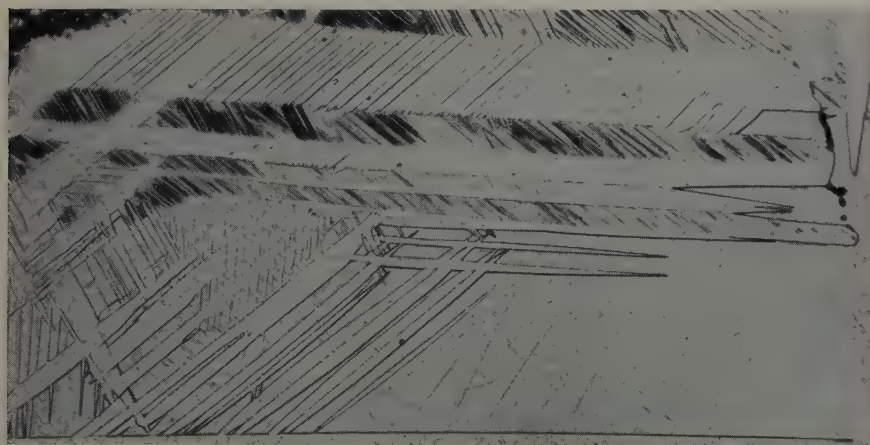


Fig. 15—Banded structure in unrepresentative surface layer of 48 atomic pct Co-Pt alloy disordered at  $950^\circ\text{C}$  then cooled to  $822^\circ\text{C}$  and held 25 hr and water quenched. Ordered plus disordered phases. X500.

Area reduced approximately 40 pct for reproduction.



Fig. 16—Widmanstatten pattern (left) and striations (right) in 54 atomic pct Co-Pt alloy held 50 hr at  $728^\circ\text{C}$ . Ordered plus disordered phases. X500.

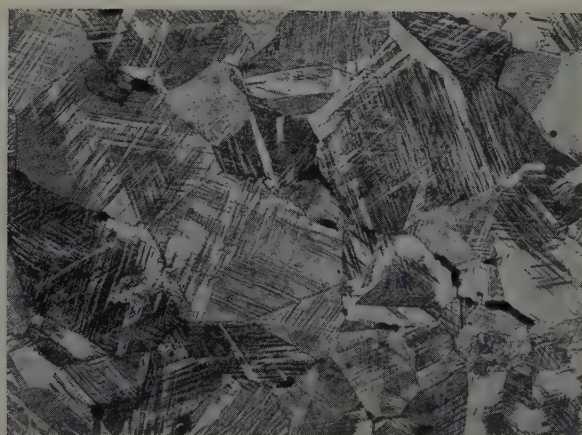


Fig. 17—Striations in fully ordered sample of 54 atomic pct Co-Pt alloy held 1000 hr at  $600^\circ\text{C}$ . X100.



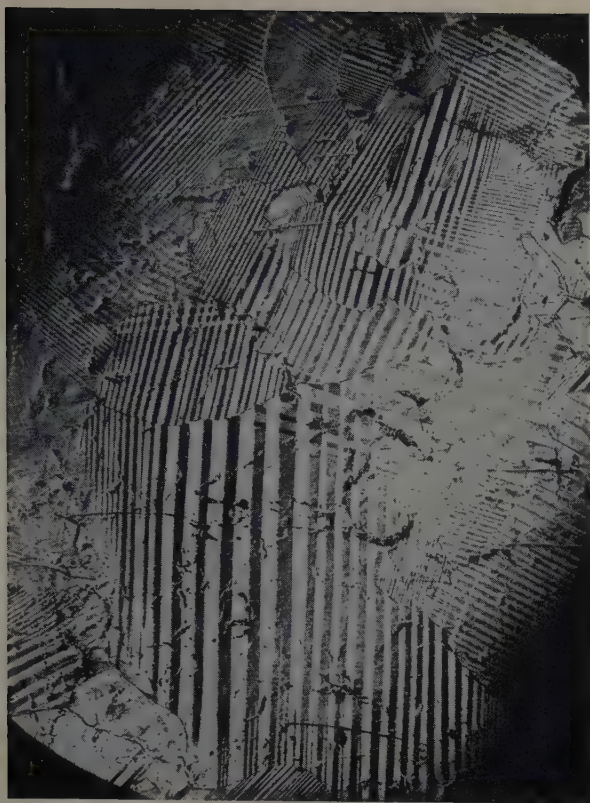


Fig. 18—Surface deformation in In-Tl alloy. Oblique illumination. X75.



Fig. 19—Same as Fig. 18, electropolished and electroetched. Area Figs. 18 and 19 reduced approximately 40 pct for reproduction.

mechanism provides a pole figure for the 20.75 pct Tl alloy, Fig. 14, in which the central portion is identical to that for the proposed double shear mechanism. Poles for the initial platelets of the tetragonal phase and first generation twins only are shown. Possibly the outer poles represent twins that do not relieve transformation stresses and thus do not occur. It might be profitable to search for these and for a Widmanstätten pattern of platelets of the tetragonal phase on  $\{111\}$  planes of the cubic phase if samples could be prepared for the two-phase structure with microscopically resolvable particles and without the structure being obscured by the banded markings.

The authors have suggested that the ordering reaction in alloys such as Co-Pt, Fe-Pt, and Cu-Au might progress by a double shear mechanism on the basis that striated microstructures are observed for these alloys also. We should like to examine the comparison further, particularly in regard to Co-Pt where we have made a rather extensive study of the microstructures. In only one sample have we observed the clear-cut main bands with sublamellae shown by Fig. 15 analogous to the structure reported by the authors for In-Tl alloys. Here all bands are parallel to  $\{110\}$  planes and the subbands are on planes at angles of  $60^\circ$  to the plane of the main band, and with evidence of interpretation. The sample which was disk-shaped as cut from  $\frac{1}{4}$  in. diam rod exhibited a transformed zone only around the cylindrical surface (see Fig. 7a, reference 15). The sample had been held at a temperature above the transformation range for the bulk alloy but below the range for the presumably impure surface layer. This sample provides an insight into the mode of lateral growth of the main bands. These usually occurred in pairs with a W-shaped edge possibly due to tilting in opposite senses as for In-Tl alloys, but frequently single main bands were observed to be growing in the untransformed matrix as in Fig. 15. The sloping surfaces at the V-shaped edges are parallel to some high order plane such as  $\{780\}$ . Possibly this should be considered as the "habit" plane rather than the  $\{110\}$  planes to which the irregular edges of the fully developed subbands are parallel.

Usually the striated structures in Co-Pt alloys are

not as clearly defined as that shown above. The more prominent striations are apparent when the transformation is conducted at temperatures in or near the equilibrium temperature range. The striations may occur in irregular nodules bounded by no distinct main bands suggesting that the "first shear" is unnecessary. In one sample a banded structure was observed in some grains (Fig. 6d, reference 14) whereas others had a clearly defined Widmanstätten pattern of platelike particles of the ordered phase in the disordered matrix (see Fig. 6c, reference 14 and Fig. 7d, reference 15). It is believed that the latter is the primitive mechanism of the transformation and this is obscured in grains so oriented with respect to their neighbors that the self-deformation process may operate. The two types of structures in adjoining grains are shown by Fig. 16. Recent analyses show that the striations also correspond to traces of  $\{110\}$  planes rather than to the previously reported  $\{111\}$  planes.<sup>14</sup> When ordering is conducted at temperatures such as  $700^\circ$  and  $600^\circ\text{C}$ , which are below the equilibrium temperature range, the striated structure is less prominent (see Figs. 7c and 7d, reference 14). Nodules of parallel bands are no longer prominent and the bands appear wavy and intersect each other very frequently as in Fig. 17. The microstructure is more similar to those which have been reported for Cu-Au<sup>5</sup> and Fe-Pt<sup>4</sup> alloys than it is to that reported for In-Tl alloys. In Co-Pt alloys the cubic phase can be retained by quenching and the transformation can be promoted isothermally at subcritical temperatures. Under these conditions the striations appear after the start of the transformation and continue to become more prominent long after completion of ordering according to X-ray data on the same metallographic samples which lend support to the hypothesis that they represent a mode of stress relief rather than the primary transformation. Finally striations are faint or absent on ordering at  $500^\circ\text{C}$  where most prominent manifestation of the transformation is the formation and growth

<sup>14</sup> J. B. Newkirk, A. H. Geisler, D. L. Martin, and R. Smoluchowski: *Trans. AIME* (1950) 188, p. 1249, *JOURNAL OF METALS* (October 1950).

<sup>15</sup> J. B. Newkirk, R. Smoluchowski, A. H. Geisler, and D. L. Martin: *Journal of Applied Physics* (April 1951).



of recrystallized nodules at grain boundaries (see Figs. 7a and 7b, reference 14).

Thus we are inclined to believe that the major mechanism of the transformation in Co-Pt alloys is by the Widmanstätten type process in which platelets of the tetragonal phase are nucleated and grow parallel to {110} planes of the cubic matrix and that the major source of striations is the self-deformation process by twinning or slipping in which strains are relieved in the course of or subsequent to the transformation.

**L. Guttman** (authors' reply: Due to the absence from the United States of the other authors, one author is responsible for the reply)—It is difficult to see why an alternative to the double-shear mechanism should be sought, since it appears to account satisfactorily for all the observations. The proposed mechanism is moreover in conflict with several critical features:

1—Presumably, a given colony of main bands consists of the tetragonal material formed by adjustments within a particular (111) plane and one of its first generations twins; but this gives only two orientations of the eight found as shown in Figs. 7 and 8, when a grain has a single set of main bands.

2—The subbands are not explained, since if they

were second-generation twins the pole clusters could not correspond to observation.

3—On the proposed mechanism, there is no way to account for the observed mode of development, which is invariably the propagation of a (110) interface into the cubic material. In the paper, it was assumed that the bands appearing on a smooth surface were identical with the "main bands" revealed by electropolishing and etching, and hence represented traces of (110) planes. Although any other possibility seemed unlikely, we have since verified their identity by comparison in several cases of the surface distortion with the microstructure of the material immediately below, as shown by Figs. 18 and 19. It should be noted especially that both members of a pair of main bands are tilted with respect to the original cubic surface (Fig. 5, reference 1), and hence that at least part of the transformation must occur homogeneously.

4—It seems rather perverse to describe the banded markings as "obscuring" the structure when in fact they have served so well in elucidating it.

Apparently the mechanism of ordering in Co-Pt alloys is more complex than suggested by us on the basis of earlier information.

## Interface and Marker Movements in Diffusion in Solid Solutions of Metals

by Luiz C. Correa da Silva and Robert F. Mehl

DISCUSSION, A. H. Geisler presiding

**A. D. Le Claire and R. S. Barnes** (*Atomic Energy Research Establishment, Harwell, Didcot, Berks., England*)—This much awaited paper admirably confirms that the Kirkendall effect is a true diffusion phenomenon and likely to be found in all diffusing systems. The most likely explanation put forward so far to account for the shift of interface is that the two components of the system, diffusing in opposite directions, do so with unequal rates so that there is a net loss of material from that half of the diffusion zone rich in the more rapidly diffusing component. This loss is accompanied, and at least partly compensated for, by a closing up or decrease in volume of this latter half of the diffusion zone and an expansion of the other half so as to tend to keep constant the overall volume per atom. This is manifest as a movement of the original interface. If this is a true picture of what is taking place then there are at least two important matters requiring further study.

1—The quantitative relating of the observed shift with the independently measured separate diffusion coefficients of the two diffusing species.

2—A detailed study of the mechanism and characteristics of the closing up process.

We would like first to make a few remarks pertinent to these topics. In connection with the first of these, it is a pity that more and detailed measurements were not made on the Au-Ag system, the only one for which the separate diffusion coefficients of the two species have been measured.<sup>18</sup> One of us (A. D. Le C.) has calculated from Johnson's results the shift to have been expected in samples D.2 and D.3. Darken<sup>4</sup> showed that the velocity  $v$  with which the markers move is related to the separate diffusion coefficients  $D_{Au}$ ,  $D_{Ag}$  by the equation:

$$v = (D_{Ag} - D_{Au}) \frac{\partial N}{\partial x}$$

where  $\frac{\partial N}{\partial x}$  is the concentration gradient at the markers. Under certain conditions,<sup>4, 20</sup> it can also be shown that:

$$v = \frac{Xm}{2t}$$

where  $x_m$  is the total marker shift after time,  $t$ :

$$x_m = 2t (D_{Ag} - D_{Au}) \frac{\partial N}{\partial x} \quad [9]$$

Johnson measured  $D_{Ag}$  and  $D_{Au}$  in a chemically homogeneous alloy and so his reported figures represent the true or ideal diffusion coefficients<sup>21</sup>; the same quantities in eq 9 represent the actual diffusion coefficients as would be measured in the presence of a chemical concentration gradient, so we need to multiply Johnson's reported values of  $D_{Ag}$  and  $D_{Au}$  by the

thermodynamic factor  $\left(1 + \frac{\partial \log \gamma}{\partial \log N}\right)$  before insert-

ing them in eq 9.  $\gamma$  is the activity coefficient of Ag at the concentration prevailing near the markers which we shall assume to be  $\sim 50$  pct. The values of the thermodynamic factor for  $N = 0.5$  and the temperatures at which D.2 and D.3 were annealed were obtained from thermodynamic data quoted by Darken.<sup>4</sup>

$\partial N / \partial x$  was computed from the coefficient of interdiffusion of Au and Ag given by Johnson on the assumption that in the samples D.2 and D.3, the concentration distance curve could be represented by the standard equation:

$$N = \frac{N_0}{2} \left\{ 1 - \phi \left( \frac{x}{2\sqrt{Dt}} \right) \right\}$$

$N_0$  is the original difference in concentration between the two halves of the couple, and  $\phi$  is the error or probability function.

$\partial N / \partial x$  at  $x = 0$  is then given by:

$$\partial N / \partial x = \frac{N_0}{2\sqrt{\pi Dt}}$$

and we assume that this represents the concentration gradient at the markers, although it is probable that the figure is slightly high.

When all the appropriate quantities are inserted in eq 9, we find that the expected shifts are: for D.2, 0.0134 cm and for D.3, 0.0119 cm.

The agreement between these results and those



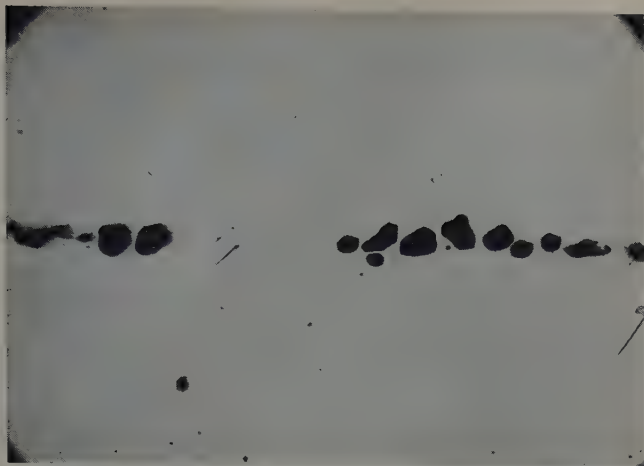
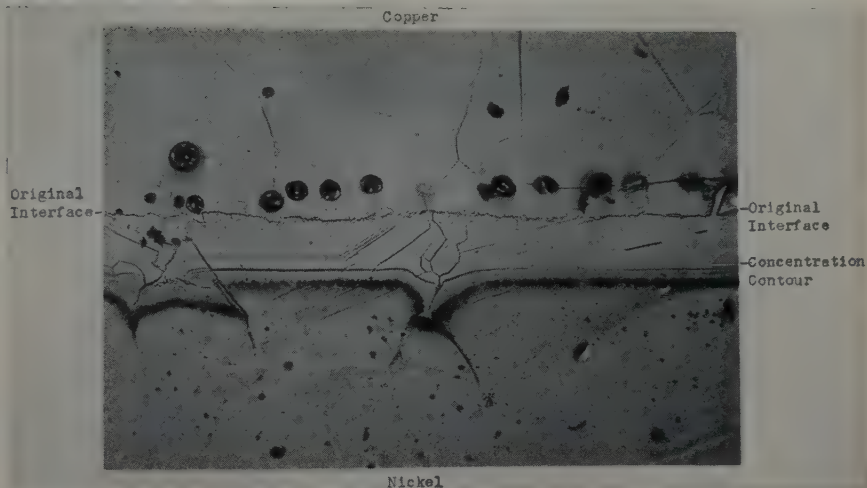


Fig. 62 (above)—Voids in diffusion zone of Cu/Ni couple diffused at 1030°C for 68 hr in hydrogen. Mechanically polished. X270.  
Area reduced approximately 75 pct for reproduction.

Fig. 63 (right)—Cu/Ni couple diffused at 940°C for 66 hr in argon. Electrolytically polished. X270.  
Area reduced approximately 70 pct for reproduction.



actually found by da Silva and Mehl is very satisfactory. It indicates that the marker movement is predominantly determined by the difference in diffusion rates; other possible sources of movement will probably only play a secondary role. Further work along these lines is much to be desired.

An important result which touches upon the closing up process is that "the Matano interface agrees with the original interface." The validity of this statement is important because it is used as evidence that porosity is negligible, although the authors did in fact find porosity. But it seems to be contradicted by the results on samples B 22-I (Fig. 17), B 39-I (Fig. 19), and B 46 (Fig. 22) where the shifts as measured using the diffusion curve method are in the opposite direction to those given in the results for the type of couple concerned. Also in this connection the result of the lateral marker experiment suggests that the shifts obtained by the diffusion curve method should be modified, so spoiling the agreement between Matano interface and original interface positions. The results of the lateral marker experiment is most interesting for not only did these markers not move together as a result of the unequal diffusion flow but, although the lattice parameter in the locality of the markers decreased, their distance apart remained constant. This result can only mean that the number of atomic planes in the direction of diffusion must increase to maintain the distance constant, and as the authors say there must be a restraint to prevent the brass from contracting in directions at right angles to the diffusion flow; this would be expected when the diffusion flow is restricted to one direction as suggested by C. S. Smith in his discussion of the paper by Smigelskas and Kirkendall.<sup>1</sup> In the light of the result of this lateral marker experiment Smith's remarks are more pertinent than before and so the shift due to lattice parameter change should be three times that plotted on the curves relating shift to  $\sqrt{t}$  or the Matano area, since the volume changes re-

sulting from the lattice parameter change can only be relieved in the direction of diffusion. If this correction is made then all the points on these plots lie under a line which is the sum of the corrected curve for the lattice parameter shift and the maximum possible shift with the remarkable exception of the results for Cu/Sn couples.

Using the same result that the movements are restricted to the diffusion direction, the lattice plots (Figs. 13 to 24) should be modified, if the effect of the change in lattice parameter is not to be included in shifts obtained by the diffusion curve method. A rough calculation in the case of the sample B 39-I, for example, would move the Matano interface to a position much nearer the ordinate. As the shift given by this diffusion curve as it stands is in the wrong direction, this correction improves the result. In all cases the correction will move the Matano interface toward the small atomic component and so increase all the shifts as calculated

from the diffusion curve (apart from those in the wrong direction, already mentioned, which will be reduced). The correction is only of importance in those couples where the Kirkendall effect is small.

It would be interesting to compare figures from the foil bend method and the diffusion curve method, for from the difference the volume occupied by voids can be estimated.

The authors of this paper found porosity in only the diffusion zones of the Cu/ $\alpha$  brass and the Cu/Al bronze couples. One of us (R. S. B.) has found quite unmistakable voids occurring in the diffusion zone of Cu/Ni couples on the copper-rich side of the original interface. Similar voids to those reported were also found in Cu/ $\alpha$  brass couples on the zinc-rich side of the original interface.

Fig. 62 shows the shape of these voids in a Cu/Ni couple which has been diffused at 1030°C for 68 hr in a hydrogen atmosphere. It may be observed that most of these voids have some straight faces which suggests that the voids are polyhedral in shape. Fig. 63 shows a similar couple, in this case diffused at 940°C for 66 hr in an argon atmosphere and given an electropolish which destroys the shape of the voids but reveals their position relative to the original interface, which is made visible by the impurities occurring in the welded join. Both micrographs show that the voids form in a fairly definite plane at right angles to the diffusion flow and, as reported for the brass couples, at some distance from the original interface, but in the diffusion zone.

In Fig. 63 the technique of outlining a concentration contour on the nickel-rich side of the original interface, as previously described,<sup>22</sup> has been used to show the preferential diffusion of the copper along the nickel grain boundaries, and in these regions where the extra diffusion has taken place the marker interface can be seen to bulge towards the copper-rich side, so giving a larger Kirkendall shift in these regions.



The grain boundaries in the diffusion zone pay little attention to the marker interface in these Cu/Ni couples, but many of them are irregular and suggest strain in this region.

The fact that visible voids are formed in certain cases suggests that the large number of vacancies involved do not necessarily condense only by the mechanism proposed by the authors. There are several possible ways in which the vacancies might condense: 1—by diffusing to the surface, 2—on dislocations with a Taylor-Orowan characteristic (within the crystal or at grain boundaries), 3—on impurities of a macroscopic or even atomic nature, 4—initially probably as plate-like voids which soon collapse producing a dislocation ring as the authors suggest, and 5—as voids which do not collapse, probably of a roughly spherical shape.

Mechanisms 1, 2, and 4 do not lead to the formation and growth of visible voids, but it is conceivable that 3 and 5 might do so, and these may be operating in those cases where voids are seen. The presence of gas dissolved in the metal might seriously affect the behavior, subsequent to their formation, of the voids produced by any of the mechanisms 3, 4, or 5 but particularly in cases 3 and 5. Once a cavity is formed by any of these mechanisms, gas present in solution in the metal might diffuse into the cavity and prevent its collapsing, when in the absence of any gas it might have done so. Once stabilized in this way, the cavities might then grow to a visible size by condensation at them of further vacancies. The authors mention the importance of gas reactions as a possible complicating feature of this type of experiment and say that this can be avoided, but without saying exactly how. In view of the existence of a porosity in some samples but not in others, it would be interesting to know if an analysis of the gas content of the samples used by the authors is available. High metallic purity of the samples seems to be no guarantee of the absence of a gas reaction as evidenced by sample C.17. It is possible also that the existence of a porosity in our Cu/Ni samples and its reported absence in those samples used by the authors may be connected with their possible different gas contents.

In connection with Fig. 39, if the values of  $D$  previously found by Rhines and Mehl, are "highly approximate," why were they included in this figure? If only the authors present results are used in calculating  $Q$ , the values at high zinc concentrations are considerably raised, to about 40,000 cal per mol, and are in much closer agreement with previous measurements of  $Q$  in high zinc  $\alpha$ -brasses.

**L. C. Correa da Silva and R. F. Mehl** (authors' reply)—The discussion of Messrs. A. D. LeClaire and R. S. Barnes is most interesting, and deserves detailed reply.

Their calculations of marker shift and the agreement of this with the observed shift in the Ag-Au system is encouraging. There are limitations to the application of the calculation, for the data are not quite adequate for the purpose: the data of Johnson are for the 50:50 composition; and the thermodynamic data employed were selected for this composition; the marker, however, surely does not follow this composition, but one at a much higher percentage of Ag,—the agreement

found is thus presumably somewhat fortuitous. The "pity" in all research lies in its necessary incompleteness. It would be good to expand the data for the Ag-Au system, for marker shift, as well as for the separate diffusion coefficients by the use of tracers—it is a bit surprising that Johnson's work has not been extended.

Porosity in diffusion samples is often a fugitive, evanescent phenomenon. Although invariably observed in Cu/ $\alpha$  brass couples, its occurrence in other couples is sometimes debatable. In most cases it is slight to the point of uncertainty; etching exaggerates it (and may change the geometry of the separate pores, as may polishing), and through the formation of etch pits may deceptively simulate it. Certainly even in Cu/ $\alpha$  brass couples the total volume of porosity is small, judging from direct observation, apart from the argument arising in the concurrence of the original interface and the Matano interface. It should be noted in passing that the contradictory results on samples B 22-I, B 39-I, and B 46 should not be given much weight; the concentration range is small, and small errors in chemical analysis disturb the results in these systems; these curves are less reliable than the others. No determinations of "gas" content were, nor could have been made on samples such as those employed. Obvious swelling was observed in some samples (subsequently discarded), originating in the generation of internal blowholes. Inert gas ambients are always to be preferred for this reason. The "foil-bend," the "reference-to-foils," and the "diffusion curve" methods avoid the difficulties which gas or any porosity creates in analysis of marker shift.

The use of lattice units did appear to us to be fundamentally justifiable, apart from any consideration of marker shift; the point which Messrs. Le Claire and Barnes make received much attention in our thinking, but in view of the fact that we have but one measurement of lateral dimensions (made late in our work) it hardly seemed useful further to develop the lattice unit scheme—or any other framework. The matter of changes in lateral dimensions in samples such as ours and in others of differing geometries ought to be studied in detail.

The new observations reported on Cu/Ni couples are most interesting. The greater marker shift near grain boundaries, where diffusion is greater, is of course to be expected. Etching techniques such as those employed have been reported before; several instances were noted in 1936 Institute of Metals Lecture, though the combination of this technique with observation of marker movement is new and might be further exploited. In our case, the grain sizes were so very large that the marker movements recorded must have been near to those for single crystals.

The five possible ways in which vacancies might condense, as suggested, have all been considered. The first seems unlikely for the reasons given in the text. The whole question of mechanism of vacancy condensation is still worthy of thought and resultant experiment; it surely is not yet satisfactorily resolved.

The text with reference to Fig. 39 must have been misread. The expression "highly approximate" was used in reference to the  $Q$ -values of Rhines and Mehl; at high temperatures, the  $D$ -values, as reported here, agree with those of Rhines and Mehl quite well, as Fig. 38 demonstrates.

<sup>20</sup> A. D. Le Claire: Discussion on reference 4, p. 194.

<sup>21</sup> Chapter 7 of reference 6.

<sup>22</sup> R. S. Barnes: *Nature* (1950) 166, p. 1032.

## Torsion Texture of Copper

by W. A. Backofen

DISCUSSION, J. R. Low presiding

**W. R. Hibbard, Jr.** (*General Electric Co., Schenectady, N. Y.*)—Dr. Backofen's pole figures showing the deformation texture of severely twisted polycrystalline copper are very interesting because of the large shear strains, the difficulty of interpretation, and their correlation with flow.

It is my opinion that the interpretation of the pole

figures given in the paper is not self-consistent. It is not reasonable to have one of the four octahedral poles of a given orientation in an area of high intensity, while the others are in areas of low intensity as is the case in Fig. 6. If the texture is (112)  $[11\bar{1}]$ , and a density of eight occurs in the longitudinal direction, then a density of eight must occur in the other positions for the octahedral poles of that orientation, or that is not





Fig. 10—Single crystal of  $\alpha$  brass with (111) plane perpendicular to the torsion axis (axis vertical, plane horizontal) given 1.68 shear strain in torsion showing slip lines and deformation bands. Polished prior to twisting. X10.

the orientation involved. The most consistent interpretation of Fig. 6, in my opinion, is a duplex texture as follows:

111 direction parallel to the longitudinal direction with a random orientation of poles perpendicular to that direction (similar to the wire texture)

(110) [001] orientation superimposed

This interpretation will account for the three high density octahedral areas and not require octahedral poles in low density areas. It can be critically evaluated by examining the (002) reflection ring and determining whether or not there are any grains actually oriented with their 001 poles parallel to the longitudinal axis. For both of these orientations slip systems are suitably oriented with slip directions in the direction of maximum shear stress to account for the required flow on the basis of the theory presented in reference 7.

The significance of this duplex texture might be explained on the basis of experiments conducted in 1947 at Hammond Laboratory by Dr. R. E. Swift at the request of Professor C. H. Mathewson. The theory of stable textures described in reference 7 indicates that if a single crystal is deformed in the texture orientation, deformation will occur without changing this orientation. A torsion specimen was prepared from a single crystal of  $\alpha$  brass with an octahedral plane perpendicular to the torsion axis (111 direction parallel to the longitudinal direction in accordance with the first orientation listed above) and the specimen was given a shear strain of 1.68 in torsion. Unfortunately, here too, the provision for free torsion did not function and the specimen was also subjected to axial compression. The appearance of slip lines on the surface (Fig. 10) indicated that most of the deformation occurred by shear on the octahedral plane perpendicular to the torsion axis leaving the 111 direction essentially parallel to the longitudinal direction and substantiating the suggestion that this is the stable end orientation or texture for the torsion of face-centered cubic metals. This orientation is the same as the wire texture with a random range of orientations from 110 to 112 normal to the stress axis. In addition to these slip lines there were several deformation bands emanating from the grip ends and extending in a slow helix toward the center of the specimen (also shown in Fig. 10). In these deformation bands the slip lines were about 50° from those in the

matrix within 5° of where they should be for a (110) [001] orientation. It was my opinion that these deformation bands were the result of the stress complexity caused by the lack of free torsion or axial compression component, and that they would not have been there under pure torsion. There is the suggestion of the start of such a band in the upper right corner of the left micrograph of Dr. Backofen's Fig. 8.

It is my suggestion, therefore, that the texture for the pure torsional deformation of face-centered cubic metals is the same as the wire texture, namely 111 direction parallel to the torsion axis and a random range of orientations from 110 to 112 normal to it; and that lack of free torsion or the compression component in the torsion axis causes deformation bands to form of the orientation (110) [001].

**W. A. Backofen** (author's reply)—Dr. Hibbard suggests that the interpretation of the pole figures is not self-consistent because all of the octahedral poles associated with an ideal orientation do not fall in equally dense areas. This is certainly a significant comment, but it seems that it might be extended to other comparably accurate pole figures describing some of the more common cold-working textures. Fig. 11 is a (111) pole figure of cold-rolled copper which was constructed with the technique developed by Norton<sup>12</sup> and discussed in connection with Fig. 6 of the paper. The orientations included in this figure, while they do not position octahedral poles in equally dense areas, constitute the accepted description of the texture.

Dr. Hibbard's interpretation of the pole figures is particularly attractive because of its simplicity. But the writer avoided choosing the [111] wire texture with rotational symmetry about the torsion axis, for if this were developed it would seem that any direction from [110] to [112] in a (111) plane might act as a slip direction.

A slip direction could be expected to coincide with the transverse direction of maximum shear-stress, but it should be unnecessary for active slip planes to be oriented only perpendicularly to the torsion axis as the [111] wire texture would imply. It should be possible to rotate a slip plane originally perpendicular to the torsion axis about the active [110] slip direction without creating an unstable texture. By the rotation, the overall texture is broadened and the (111) [112] and (110) [001] orientations can be derived from the (112) [111]. It is not easy to rationalize the ideal texture (112) [131], which can be obtained very nearly from the (111) [112] by a 20° rotation about a [110] direc-

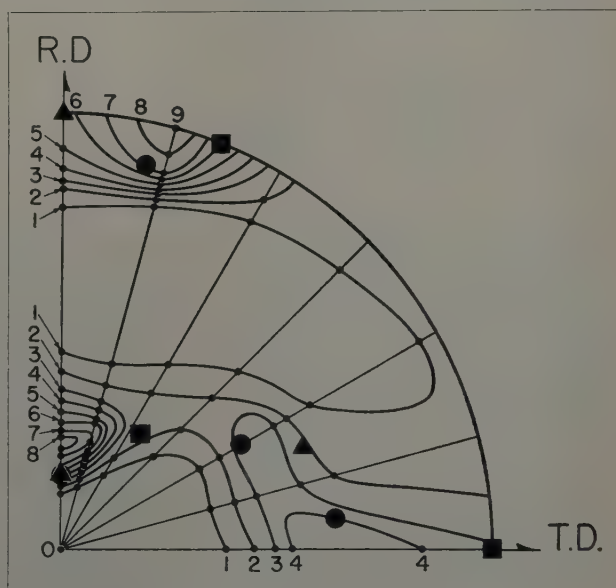


Fig. 11—(111) pole figure of OFHC copper reduced 95.5 pct in thickness by cold rolling.

Ideal orientations: solid square—(110) [112]; solid triangle—(112) [111].



tion lying in the plane of Fig. 7 and inclined 30° from the longitudinal direction. It may be that the contribution of this orientation to the description of the torsion texture is not important enough to warrant its use.

The [100] pole distribution was examined by means of a (100) pole figure and also by measurements of the intensity of reflection from (200) planes parallel to the flat surface of disk-shaped specimens removed from some torsion bars. These specimens were prepared so that their flat surfaces were perpendicular to the axes of the bars. It could be concluded from the information obtained in the two ways that there were some grains oriented with their [100] poles parallel to the longitudinal or torsion axis.

It is very interesting to learn that the deformation bands in the twisted single crystal described by Dr. Hibbard are of the orientation (110) [001]. These undoubtedly contribute to the overall texture. However, the pole figure of Fig. 4 was constructed from a specimen that was reasonably free from axial compression during twisting, and it is not different from the others.

This suggests that the (110) [001] part of the texture cannot be attributed entirely to deformation bands caused by the restricted torsion. Since this work was published, the axial compressive stress resulting from restricted torsion has been measured. For copper specimens used in this work, the stress rises gradually to a maximum of about 2000 psi, which is 8 pct of the corresponding shear-stress at a shear-strain of 2. It then decreases rapidly as the shear-strain increases. Thus the constraint is relatively small and again it does not seem that it is entirely responsible for the pronounced (110) [001] component of the texture.

Additional work on the torsion texture in polycrystalline  $\alpha$  brass has just been completed, but, unfortunately, the pole figures have not yet been prepared for publication. It is interesting to find that the (110) [001] orientation is a necessary, although minor, component of the texture. However, the [111] wire texture does not appear to be an adequate description of the balance of the texture.

## Effect of Ferrite Grain Structure Upon Impact Properties of 0.80 Pct Carbon Spheroidite

by M. Baeyertz, W. F. Craig, Jr., and E. S. Bumps

DISCUSSION, J. R. Low presiding

**R. M. Fisher and J. F. Boyce** (U. S. Steel Co., Kearny, N. J.)—In recent determinations of ferrite grain size in specimens of AISI-SAE 1060, deoxidized with 0, ½, 1, and 2 lb of Al per ton we found, in agreement with the authors of this excellent paper, that ferrite grain size established by tempering martensite is apparently independent of prior austenite grain size over a considerable range. We felt that others might be interested in our experiences with martensite tempered for shorter times, in which the spheroids were much smaller and much more closely grouped than those in the authors' specimens.

We found it difficult to estimate reliably ferrite grain

size with the optical microscope in specimens quenched from 1650°F, tempered for 1 hr at 1250°F, and etched with nital of various concentrations up to 5 pct. A typical micrograph of an aluminum-free specimen after this treatment is shown in Fig. 21a. Austenite grain size was ASTM No. 3 in this steel and No. 7 in those containing aluminum.

It was hoped that the X-ray diffraction technique described by Clark<sup>6</sup> would permit accurate measurement of ferrite grain size. However, continuous rings rather than individual spots were formed, which indicated merely that the ferrite grains were finer than ASTM No. 11.

Finally we resorted to the electron microscope and found that by etching these specimens in 2 pct aqueous ammonium persulphate solution for 10 sec, followed by 3 pct nital for 5 sec, we were able to observe ferrite grain size and structure. Collodion replicas, shadowed with uranium, were made of all four specimens. By counting grains in micrographs representing six randomly located areas for each specimen, we found the ferrite grain size of all specimens to be ASTM No. 15, regardless of prior austenite grain size or amount of aluminum addition. A portion of a typical electron micrograph of the replica from the aluminum-free specimen is shown in Fig. 21b. It should be noted that the etchant used shows the ferrite grains primarily because of differences in appearance of the surface of adjacent grains rather than by outlining grain boundaries.

<sup>6</sup>G. L. Clark: *Applied X-rays*, p. 504, 3rd Edition (1940) New York. McGraw-Hill Book Co.

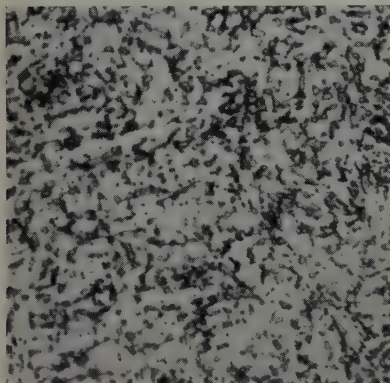


Fig. 21a (left) — Tempered martensite, 1 hr at 1250°F. 5 pct nital etch. X2000.

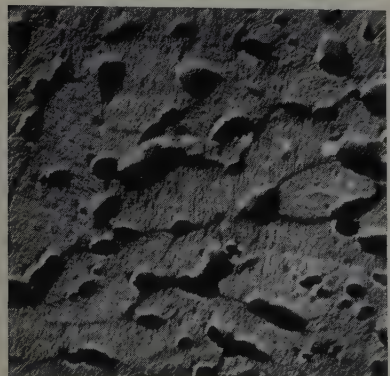


Fig. 21b—Tempered martensite, 1 hr at 1250°F. Ammonium persulphate and nital etch. X9000.

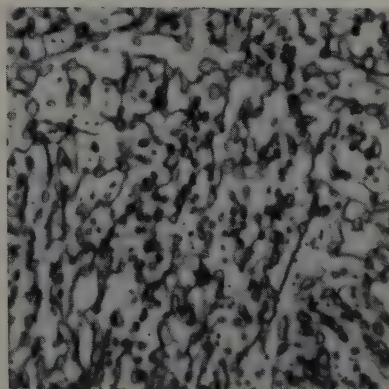


Fig. 21c—Tempered martensite, 19 hr at 1250°F. 5 pct nital etch. X2000.

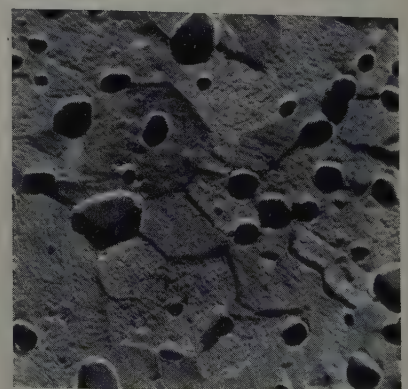


Fig. 21d—Tempered martensite, 19 hr at 1250°F. Ammonium persulphate and nital etch. X7000.



To investigate whether ferrite grain boundary delineation would be improved by longer tempering, the aluminum-free specimen was heated an additional 18 hr at 1250°F (Figs. 21c and d). Ferrite grain size was again determined by counting the number of grains in the known area of electron micrographs and was found to be ASTM No. 13.5, a five fold increase in volume.

The grains in the electron micrograph (Fig. 21d) appear more equiaxed than those in the optical micrograph (Fig. 21c). This seems to indicate that some of the elongated grains, observed with the optical microscope after etching with nital, consist of more than one equiaxed grain, but that nital failed to outline all boundaries adequately.

It was found that altogether 5 pct nital was not as satisfactory with the electron microscope as ammonium persulphate plus nital, ammonium persulphate plus nital was not as satisfactory as 5 pct nital when etching for the optical microscope.

We conclude that ferrite grain size may be measured by using the electron microscope and an ammonium persulphate plus nital etch, when it is difficult to outline grain boundaries satisfactorily for the optical microscope.

**M. Baeyeritz** (authors' reply)—The authors are grateful for the added information on ferrite grain structure presented by Messrs. Fisher and Boyce. When the ef-

fect of composition on ferrite grain growth as well as the influences of temperature and period at temperature are taken into account, the evidence in the optical and electron micrographs of the discussers seems to be in agreement with the optical observations of the authors. The ferrite grains in Figs. 21a and b are elongated and of the shape that might be anticipated from a martensite plate structure, but as stated in the discussion, considerable equiaxing and some growth of the ferrite grains was observed after treatment for 19 hr at 1250°F. With the 0.80 pct C-1 pct Ni steel used by the authors, the spheroidization treatment of 54 hr at 1150°F caused but very slight ferrite grain growth, so that the ferrite grain structure after this treatment was essentially the same as that observed with shorter periods of spheroidization at the same temperature. The difference in the rate of ferrite grain growth in the discussers' AISI-SAE 1060 steel and the authors' 0.80 pct C-1 pct Ni steel is ascribed to the differences in composition and spheroidization temperature used in the two cases.

We agree that electron microscopy is a useful tool for study of ferrite grain structures when used with the technique applied in the discussion. Because of the smaller field represented by any one electron micrograph, care must be taken to compare larger fields by light microscopy.

## Effect of Alloying Elements on True-Stress True-Strain Flow Curves of Pearlitic Steel

by R. Raring, J. A. Rinebolt, and W. J. Harris, Jr.

### DISCUSSION, J. R. Low presiding

**G. W. Geil** (National Bureau of Standards, Washington, D. C.)—The authors state that the degree of accuracy realized in the experimental determination of  $\sigma_f$  is likely rather low. This inaccuracy is attributed to the difficulty in reading the load of the tension machine at the instant of fracture of the test bars. I believe there is another factor which may have added considerably to the inaccuracy in the determination of  $\sigma_f$ , namely, the determination of  $\delta_f$ . Fracture of a cylindrical tensile specimen of a ductile metal tested in tension at room temperature is generally initiated at the axis and rapidly propagates radially to the periphery of the necked section. During the propagation of the fracture, the metal at the rim of the minimum cross-section extends longitudinally and contracts radially. Thus values of  $\delta_f$ , based on diameter measurements

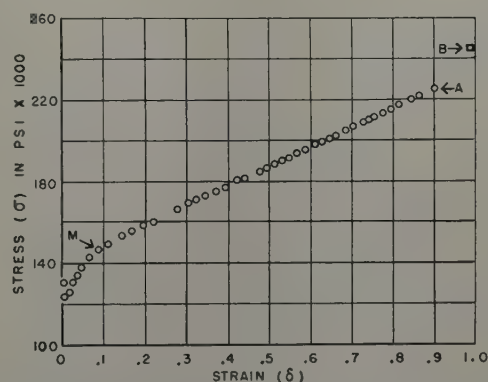


Fig. 13—True stress-strain curve for a specimen of 0.3 pct C steel in the condition as-quenched from 1575°F and tempered 1 hr at 1000°F and tested in tension at 80°F.

M—values at maximum load. A—values based on diameter measurement at initial fracture. B—values based on diameter measurement after fracture.

Table V. Extent to Which Terminal Points Lay Above (+) or Below (—) Flow Curve

| Steel | Deviation, psi | Steel | Deviation, psi |
|-------|----------------|-------|----------------|
| C1    | −1000          | Cu1   | −3000          |
| C2    | +1500          | Cu2   | + 500          |
| C3    | +3000          | Cu3   | + 500          |
| C4    | 0              | Cu4   | +2000          |
| C5    | +1000          | Cu5   | 0              |
| C6    | 0              | Cr1   | −3500          |
| C7    | 0              | Cr2   | +7000          |
| Mn1   | −2000          | Cr3   | +10,000        |
| Mn2   | −3000          | Ni1   | 0              |
| Mn3   | +1000          | Ni2   | − 500          |
| Mn4   | +8000          | Ni3   | +2000          |
| Si1   | 0              | Ni4   | +8000          |
| Si2   | + 500          | Ni5   | 0              |
| Si3   | −2000          | Mo1   | −1000          |
| Si4   | −2500          | Mo2   | −1500          |
| Si5   | −5000          | Mo3   | −1500          |
| P1    | −1000          | Mo4   | 0              |
| P2    | 0              | V1    | −2500          |
| P3    | 0              | V2    | − 500          |
| P4    | −4000          | V3    | + 500          |
|       |                | V4    | −1500          |

made after complete fracture of the specimens do not necessarily represent the strain at the initial fracture.<sup>11</sup> Data obtained at the National Bureau of Standards with a 0.3 pct C steel in the condition as-quenched from 1575°F and tempered at 1000°F for 1 hr and tested in tension at room temperature indicated a considerable "rim effect" and as shown in Fig. 13, resulted in an apparent increase in  $\delta_f$  from 0.90 to 0.98. As the fracture strain of this steel is approximately equal to those of the steels reported by the authors, it seems probable that a similar "rim effect" may have added to the inaccuracies in the reported values of  $\delta_f$  and accompanying values of  $E_f$ .

**R. Raring** (authors' reply)—The authors are grateful to Mr. Geil for having called attention to a possible source of uncertainty in the determination of fracture stress, and they are in agreement with the principles upon which his discussion is based.

<sup>11</sup> D. J. McAdam, Jr., G. W. Geil, and R. W. Mebs: *Trans. AIME* (1947) 172, p. 323; *METALS TECHNOLOGY* (August 1947).

However, it is considered that the "rim effect" in the majority of the pearlitic steels used in the investigation under discussion was negligible, and certainly less than in the quenched and tempered steel cited by Mr. Geil. This consideration is based on the fact that terminal points of the flow curves did not consistently lie above the straight line portion of the curve, as does point B in Fig. 13. It would be expected that if a marked "rim effect" occurred, the terminal points calculated from

the strain after fracture and the load at the beginning of fracture would lie above the straight line.

In Table V, the extents to which the terminal points were removed from the straight line are listed, and it can be seen that more were low (17) than were high (14), while 10 points were on the curve. Point B of Fig. 13 is approximately 15,000 psi above the extension of the curve. Thus only steels Mn 4, Cr 2, Cr 3, and Ni 4 show a marked upward deviation from the flow curve.

## Transitions in Chromium

by M. E. Fine, E. S. Greiner, and W. C. Ellis

### DISCUSSION, C. S. Barrett presiding

**C. H. Samans and W. R. Ham** (Chicago, Ill., and Dixfield, Maine, respectively)—For several years we have been studying transitions of this basic type in metals, alloys, glasses, etc. Usually, however, they are not so clearly marked as those which the authors have found, and hence are much more difficult to determine accurately. Since our studies indicate that most of them occur virtually unchanged (as far as temperature is concerned) regardless of the form in which the element appears, we believe that they are a characteristic of the atom.

Specifically, we believe that there is an additional rotational degree of freedom possessed by the nucleus which has not been considered heretofore. This nuclear rotation is made up of several components, each related to the several quantum shells of electrons. In chromium there are four of these shells and hence four separate series of characteristic transition temperatures. The lowest temperature at which any transition occurs, based on the present state of our computations, is 125°K, 4° higher than the authors' value of 121°K. A convergence of this series, we believe, shows up at the higher temperature of 2085°K, surprisingly close to the transformation temperature of 2103°K recently announced by N. J. Grant of M.I.T. for a body-centered to face-centered transformation in chromium.

Likewise, our computations indicate a temperature of 311°K for the second transition temperature, reported by the authors as 310°K. A convergence of this series, we believe, shows up at a higher temperature as the melting point at 2163°K.

Although our work on these series must, in a sense, still be regarded as empirical, since we do not understand fully as yet just what the series mean, it is based on a reasonably firm picture. The individual constants, from which the various series are computed for each element, comes directly from the X-ray K absorption limit. Furthermore, the same basic method has accounted for transformation and melting temperatures in about 50 of the chemical elements, which is all we have tried thus far. In many cases the only known transformation is the melting point, but in others the occurrence of transformations or other transitions, equally as well marked as those of the authors, has been pointed out by others. These observations have assisted us greatly. Consequently we were very pleased to see the authors' excellent work in finding these two transitions in chromium. With these confirming data, our picture of this element is clarified considerably, so we expect that at least some of our work can be published in the near future.

**R. C. Ruder** (E. I. du Pont de Nemours & Co., Wilmington, Del.)—The authors' interpretation of these transitions in terms of 3d to 4s electronic structure transitions is most interesting. It would be interesting to have additional experimental evidence of such transitions from the temperature dependence of the Hall coefficient in the neighborhood of the property changes discussed in this paper. Simple theory<sup>16</sup> suggests the Hall coefficient as a measure of the free electron (or s

electron) concentration per unit volume. It has been shown that for paramagnetic<sup>16</sup> and ferromagnetic<sup>17</sup> metals the simple theory is in fact too simple. However, the existence of a discontinuity in the Hall coefficient would provide information which should aid both in our understanding of these transitions and the significance of the Hall coefficient in these metals. It was rather surprising that no significant paramagnetic effects were observed. In this connection the recent work of McGuire and Kriessman<sup>18</sup> is cited. They measured the magnetic susceptibility of chromium from 20° to 1460°C. They also observed no large change in the susceptibility although there might be a change in slope in the vicinity of the 40°C transition.

The existence of these 3d to 4s electronic transitions has been discussed in connection with the paramagnetic susceptibility behavior of nickel and nickel alloys.<sup>19-21</sup> Assuming a correspondence principle between classical and quantum mechanical paramagnetic theory and using classical theory to calculate the effective Bohr magneton number from the Curie constant for substances obeying the Curie-Weiss law,<sup>22</sup> it is found that the effective magneton number is a function of temperature. The process of calculation involves the inverse of the differential of the  $1/x_A$  vs. temperature curve so that good and numerous data are necessary to obtain significant results. The data of Fallot<sup>23</sup> show a discontinuous increase of about 12 pct in the effective magneton number between 850° and 900°C, followed by a continuous increase up to the melting point. The data of Sucksmith and Pearce<sup>24</sup> show a possible 8 pct increase. The older data of Terry<sup>25</sup> and Weiss and Foex<sup>26</sup> show a continuous increase. It is possible that small amounts of impurity atoms change these electronic transitions significantly. Fallot's<sup>23</sup> data on a nickel alloy with 4.5 atomic pct Fe indicate that the discontinuity occurs around 1300°C.

Systematic investigation of the transition metals for transitions of this nature should provide information which would be very valuable for our understanding of these metals.

The absence of antiferromagnetic structures in chromium has been shown by Shull<sup>27</sup> using neutron diffraction techniques.

**M. E. Fine, E. S. Greiner, and W. C. Ellis** (authors' reply)—The remarks by Drs. Samans and Ham are certainly very interesting, in particular those pertaining to the close agreement between the theoretically calculated values for transition temperatures in chromium and the experimental values reported by a number of investigators. This is a remarkable achievement and we shall look forward to a more detailed presentation of the method followed in their calculations.

We do not believe that the transition in pure chromium near 40°C remains temperature invariant with alloying, as was reported by Samans and Ham for a number of the substances that they studied. We have not done any work with alloys but base our belief on the results of earlier studies in which less pure chromium was included and considerably lower transition temperatures were observed. The transition tempera-



ture, it would be expected, would be changed by solid solution alloying through modification of the electron distribution in the chromium atom by the neighboring solute atoms. The transition is still primarily a property of the chromium atom.

We appreciate Dr. Ruder's discussion of the results of susceptibility measurements on chromium which were not available to the authors at the time the paper was presented. It is gratifying that these measurements support our conclusion that the transition near 40°C is not loss of antiferromagnetism. This seems to be confirmed by the neutron diffraction measurements subsequently reported by Shull. We agree that precise measurements of susceptibility and Hall coefficient would be of great value for filling in some of the details of this transition.

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## Lattice Parameters of Magnesium Alloys

by Robert S. Busk

DISCUSSION, M. Hansen presiding

**William Wilson, Jr.** (*Armour Research Foundation, Chicago*)—In his treatment of the relatively soluble group of alloying elements, the author has calculated the regression coefficients, and found that the  $c/a$  coefficients for gallium, mercury, and zinc are not significantly different from zero. However, the Student  $t$ -test may fail to indicate a significant difference, even if one exists, when insufficient data are tested. The same binary alloys are also those for which the minimum number of observations are available. For these cases, at least, it would be desirable to calculate the fiducial limits of this coefficient. The author's data for magnesium, showing the individual results for each of the five samples, and a knowledge of his weighting procedure in finding these regression coefficients, would be required to calculate the fiducial limits.

Although the work of the previous investigators, reviewed by Raynor,<sup>15</sup> indicates a minimum in the  $c$ -spacing vs. atomic pct curves for indium and thallium, and an inflection point in the curves for aluminum and gallium, the author's treatment precludes finding these features of the curves. If a suitable equation for these previous investigations were also tested against the data, then the standard errors of the two might indicate

the more exact treatment.

At the first reading, it may appear that the author has tested all of the lattice parameters of the relatively insoluble group with the assumption that the populations were infinite. Actually, in a novel way, the author has corrected the  $t$ -values in a way to make this a significant basis for comparison. I wonder if, in calculating the standard errors, the degrees of freedom were considered instead of the " $N$ " defined as the "number of data points."

**R. S. Busk** (author's reply)—The minimum in the  $c_0$  parameter is obtained by combining the data for the  $c/a$  ratio and the  $a_0$  parameter. The  $c/a$  ratio was considered more fundamental and was therefore studied more exactly. In those cases having a minimum in the  $c_0$  parameter, the equation does not reduce to the value of pure magnesium at zero concentration. It is therefore evident from this alone that there is a break of some type in the curve. If the  $a_0$  parameter is decreasing while the  $c/a$  remains constant, then the  $c_0$  must also decrease.

The standard errors were calculated by using  $N$  rather than  $N-F$ .

<sup>15</sup> B. R. Chalmers: *Progress in Metal Physics*. Vol. I, p. 69 (1949) Interscience Pub. Co.

## Intergranular Energy of Iron and Some Iron Alloys

by Lawrence H. Van Vlack

DISCUSSION, H. L. Burghoff presiding

**C. S. Smith** (*University of Chicago, Chicago*)—The author is to be congratulated on his valuable contribution to the extremely meager absolute data on interface energies in metallic systems.

It is interesting to note that the ratio between  $\alpha$  and  $\gamma$  iron boundary energies is approximately the same in the quaternary alloy with silicon, carbon, and sulphur as in the binary Cu-Fe alloy. A value for the copper grain boundary energy can be obtained from the author's data, Tables IV and VI, by utilizing the energy ratios of the following pairs of interfaces: copper-sulphide/copper, copper  $\gamma$  iron,  $\gamma$  iron/ $\gamma$  iron,  $\gamma$  iron/

copper, and copper/copper. This gives a value of 595 erg per sq cm for the free energy of the copper grain boundary. Despite this circuitous route and the assumption that the  $\gamma$  iron boundary is identical in alloys with and without sulphur and does not change between 1105° and 1000°C, this figure is in remarkably close agreement with other values of the copper boundary energy, obtained by equilibration against lead and against the free copper surface. It therefore appears either that impurities do not greatly affect the grain boundary energies or that boundaries in even nominally pure metals are already sufficiently contaminated so that further change has little effect.

# Formation of Annealing Twins

by J. E. Burke

DISCUSSION, H. L. Burghoff presiding

**R. G. Treuting** (*Bell Telephone Laboratories, Murray Hill, N. J.*)—A growth-accident hypothesis of annealing twin formation raises a question which may deserve clarification. In heavily anneal-twinned material such as  $\alpha$  brass, parallel-sided twin bands are by far the predominant form observed. This requires for the present theory that following one growth accident to generate a twin orientation, the most probable subsequent growth accident be on an octahedral plane of the same set, i.e., parallel to the existent composition plane. The implication is twofold: first, that the direction of grain growth remains the same for original and twinned components; and second, that this still advancing octahedral plane (now rotated about its own pole by twinning) remains the most likely to meet an aggregation of atoms suitably disposed for another accident.

The first condition seems to impose little difficulty. The evidence advanced by Dr. Burke indeed supports the choice of  $\langle 111 \rangle$  as a favored growth direction, and this would not be altered by the twin accident. Yet there are three other  $\langle 111 \rangle$  symmetrically arranged about that operative in an accident. Although subsequent twinning does occur about one of these alternative poles from time to time, one particular set of octahedral planes is more often consistently favored, as shown by successive parallel twin bands. After a twinning accident, the operative set of planes should have by far the largest area of the four in the twinned material. It may then be that its probability of encountering an orientation suitable to further twinning is correspondingly larger even though growth may be proceeding at the same rate in all four  $\langle 111 \rangle$  directions. I do not know that this explanation is adequate and would appreciate any comments from the author.

I should like to offer two tentative suggestions with respect to points Dr. Burke considers unresolved:

1—He has already noted grain boundaries as a discontinuity likely to cause twinning during grain growth. The frequency with which a growing grain meets a new orientation that may permit twinning is then a function of the then prevailing grain size. The relative constancy of twin density (twins per grain) throughout grain growth may be related to this. That is, the larger the grain size, the less often a twin accident is likely to occur.

2—It is possible that when a growing grain meets an orientation nearly suitable for a twin accident, whether or not this occurs may be controlled by the states (e.g., the surface energies) of the incident planes. The intensity of twinning may be related in this manner to the presence of solute atoms and so vary among alloys. This, to be sure, is not a crystallographic argument and perhaps does not lie within the intended scope of Dr. Burke's paper.

**W. G. Burgers** (*Technische Hogeschool, Delft, Netherlands*)—The subject of Dr. Burke's highly interesting paper is one which has been occupying me (and probably other metallographers) considerably during the last years. The two main possibilities, brought forward in the paper to explain the formation of annealing twins, viz: 1—the mechanical nucleation hypothesis, and 2—the growth fault hypothesis, have been discussed.<sup>13, 14</sup> In these papers direct experimental evidence was given by means of the "electron emission loupe" for the fact, mentioned in Dr. Burke's paper, that the width of twin bands bounded by parallel sides remains unchanged. In this investigation by means of the electron emission image a cinematographic record was obtained of the growth, by "exaggerated grain growth" ("secondary recrystallization") of nickel-iron foil, which shows clearly that twin lamellae grow

parallel to their straight boundaries (cf. Fig. 8). This fact, which is also clear from Dr. Burke's Fig. 4, seems therefore well established.

The idea that the condition for twins to grow wider is to have a grain boundary as one side, seems to me very stimulating, also the evidence that twins usually form at or near the corner of grains. In this connection the explanation brought forward in a recent note by Fullman<sup>15</sup> is of the greatest interest.

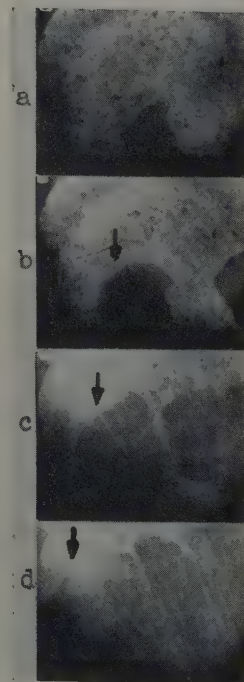
The suggestion given there, due to J. C. Fisher, "that an annealing twin forms in the corner of a growing grain when the orientation relationships between the twin and the grain's neighbor lead to a smaller total interfacial energy than do the orientation relationships between the grain itself and its neighbors," makes it in principle understandable: 1—that twin formation is of necessity related to "lattice faults" (grain boundaries included), which explains why the same metal can "crystallize" without considerable twinning (for example when crystallizing from the melt), 2—that the frequency of twinning depends to a large extent on the "texture" of the matrix in which recrystallization or grain growth takes place, and 3—that different cubic face-centered metals, like copper and aluminum, may differ so much in their twinning frequency as a consequence of a different degree of anisotropy of surface grain boundary energy.

With regard to the above suggestions, I should like to point out that for some time I thought that a somewhat different mechanism, to some extent related to the growth fault hypothesis, might account for them. Although I feel inclined at present to consider a mechanism as proposed by Fisher to be more probable,\* yet I cannot give up this idea completely.

The starting point for my considerations<sup>16</sup> was the formation, observed when recrystallizing fine grained aluminum by "primary recrystallization," of "pointed grains" (like B in Fig. 9), the lattice of which appeared to be in exact spinel-twin position (within at least 1

\* I must confess that, although grasping the general idea underlying Dr. Fullman's short note, I find difficulty in deducing from the figure given how the atomic processes leading to the twin formation should be visualized.

Fig. 8—Electron optical observation of the formation of twin lamellae of constant width during growth of a large crystal in nickel-iron foil by "secondary recrystallization" (from references 13 and 14). X25.





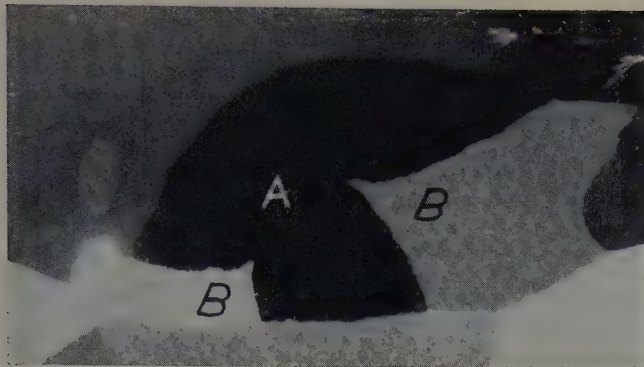


Fig. 9—"Pointed" twins (B) formed by "stimulation" by crystal A. Natural size. Area reduced approximately 40 pct for reproduction.

min of arc<sup>17</sup>) with regard to the lattice of the "surrounding crystal" (A in Fig. 9).

It was shown that the occurrence of such point-shaped crystals can be understood on the assumption that growth of such a "stimulated" crystal starts at the moment that an already growing "stimulating" crystal comes into contact with its nucleus, which was supposed to be a lattice region of the original matrix. In connection with the observed precise twin relationship existing between both crystals, it was thought possible that, on such encounter, "elimination" of a set of dislocations at the plane of contact, by mutual annihilation of dislocations of opposite "sign" (opposite "sense" in case of screw-dislocations) might cause a release of strain energy in the contacted lattice domain, which thus might be transformed into an active nucleus itself. Of course the frequency of such an event would depend largely on the texture of the matrix, as it would be controlled by the chance of a growing crystal to meet a lattice region in "precise" twin position, which it could stimulate to growth. In agreement herewith it was found that even in the same metal, in this case aluminum, the frequency of such twin formation depended very much on the texture of the matrix and varied from case to case.

On the basis of these experimental facts it was thought possible that the frequent twinning in metals like copper, nickel-iron, etc. might be due to the circumstance that the new crystals often develop in a matrix with a fairly pronounced texture, for example the cubic texture in the case of secondary recrystallization of annealed rolled foil. Moreover, as we know from various investigations,<sup>7</sup> these new crystals occupy positions which are related to the matrix texture by rotations about an axis normal to an octahedral plane. Although the amount of rotation, according to most investigators, differs from that observed for exact twinning, it must be kept in mind that these data are deduced by comparing the positions of the new crystals with the "centers" of the pole figures of the matrix. As these latter do generally show a considerable degree of scattering, it seems, a priori, not impossible that the crystals in the course of their growth repeatedly met individual grains of the matrix, which, with regard to them, occupy exact twin positions. In such cases, according to the suggestion given here, stimulation could take place, thus causing a lattice element of the disappearing texture to grow in exact twin position with regard to the already growing crystal, and so forming an "annealing twin." It is evident, however, that this mechanism, when occurring in a pronounced texture, would lead principally to a family of twins corresponding to the matrix-texture; whereas, as Dr. Burke points out, frequently examples of grains with several families of twins are observed.

In annealed rolled aluminum, where, according to Beck and coworkers,<sup>20</sup> similar orientation relationships between matrix and new crystals hold, the fine grained texture is generally less pronounced than in copper or nickel-iron. This, I thought, might explain, why, in aluminum, the "twins" have in general curved bound-

aries (cf. Fig. 9), as contrasted to copper, etc., where straight edges are generally formed. In fact, the "curved" twins in aluminum grow in matrices with an only slightly pronounced, or even nearly random, texture, so that the boundary-orientation relationship between growing grain and matrix changes from grain to grain; whereas in copper, etc., the texture is generally far more pronounced, possessing for example the "cube-texture," so that growth conditions will remain more constant over longer distances. I must say, however, that I feel not quite clear with regard to this point. In any case, it is a fact that, on recrystallizing a deformed aluminum matrix with a pronounced texture, obtained by rolling a single crystal, "twins" with straight edges are also formed;<sup>21</sup> whereas, on the other hand, the large copper crystals obtained by Cook and Macquarie<sup>22</sup> in cross-rolled copper by "abnormal grain growth" (which has a more random texture than foil rolled in one direction only) show many curved boundaries.

In order to have a direct test that the frequency of twin formation depends upon the orientation relation between growing grain and matrix texture, use might be made of the method of growing a crystal "round the corner," as applied by Tiedema<sup>23</sup> for the preparation of large aluminum crystals with a definite orientation with regard to the surface directions of the test-piece (which method is closely analogous to that applied by Dunn<sup>24</sup> and coworkers for preparing iron-silicon crystals with definite orientations): if in a fine grained matrix with a fairly sharp texture, we start growth of a large crystal at one end by pulling it partly through a heating zone, then bend the not yet recrystallized part and proceed with the growth of the large crystal "round the corner" by now passing the whole test-piece through the heating zone, then we may expect that the frequency of twinning is different at both sides of the "bent," as the relative position of growing grain and to-be-consumed matrix is different before and after passing the "bent." We intend to carry out this experiment. Of course, in case the above expectation comes true, this experimental fact is not exclusively in favor of the "stimulation" theory; it might also be expected on the basis of the views given in Dr. Burke's and Dr. Fullman's papers.

**J. E. Burke** (author's reply)—I should like to thank Professor Burgers and Dr. Treuting for their kind and stimulating discussion of my paper. In particular, I should like to thank Professor Burgers for calling attention to his earlier discussion of these two mechanisms and to his evidence that parallel-sided twin bands do not grow in width.

The stimulation mechanism for the formation of twins which Professor Burgers has proposed is very ingenious. It might be pointed out that it cannot operate to form twins during grain growth since the strained fragments or nuclei necessary for the mechanism are not present.

On the other hand, in a deformed metal, either the stimulation or growth accident mechanism could operate. An experimental method of deciding between these mechanisms would be desirable. Professor Burgers suggests an experiment in which the frequency of twinning is observed in a grain as its orientation and growth direction with respect to a textured matrix is observed. Unfortunately, as Professor Burgers points out, a change in twinning frequency with texture could be explained by either mechanism. In fact, some evidence that the direction of growth influences the intensity of twinning was presented in this paper and used to support the growth accident hypothesis. Nevertheless, the results of the experiment will be highly interesting and will certainly help describe the conditions necessary for the formation of twins in greater detail.

I should like to suggest another experiment which might possibly allow a decision to be made between the two possible mechanisms in the formation of the pear shaped "stimulation" grains Professor Burgers shows in Fig. 8. The stimulation hypothesis requires



that the stimulated grain and its stimulator or parent have a (111) slip plane in common, and this (111) plane will, of course, be the twinning plane. In order for the dislocations to move in a proper direction, this (111) plane must be approximately normal to the interface between the two grains at the moment of stimulation. Thus it might be expected that this (111) plane would contain a line which would approximately bisect the angle of the stimulated grains.

On the other hand, if the "stimulated" grain were to have been formed by the growth fault mechanism, the twinning plane should be approximately perpendicular to the line bisecting the apex of the "stimulated" grain, that is, the (111) twinning plane must coincide with the initial interface between the "stimulated" grain and its parent.

The obvious experiment is to determine the position of the twinning plane for a number of cases of stimulation in aluminum. If its position is reproducible with respect to the apex of the stimulated grain it should be possible to draw a conclusion as to mechanism.

If it develops that the position of the twinning plane between the parent and stimulated grain is more or less random, then, unfortunately, no decision will be possible. This could result from the fragment having been partially surrounded before stimulation occurred. It could equally well have resulted from a growth fault occurring on the side of a projection on the parent grain. These should, however, be more or less random, so that if the position of the common (111) plane in a number of stimulated grains are determined, no false conclusion should be drawn.

In reply to Dr. Treuting's first question, I would agree with his explanation. Where a twinning accident occurs it indicates that a grain was growing approximately normal to that (111) twinning plane. Since the twin is in a symmetrical orientation it will probably continue to grow in the same direction, and, as Dr. Treuting points out, the greater part of its advancing front will approximate the (111) twinning plane so that it will be most probable for the next twin to form on that (111) plane and reproduce the original orientation. In further support of this explanation advanced by Dr. Treuting, I can cite Fig. 5 of the paper. Here, on the right hand side, the grain had grown a great deal before any twinning accident occurred, so the condition that the advancing front of the grain is all approximately parallel to a single (111) plane was not

fulfilled. Here, twins on two other octahedral planes formed.

To some extent I think the apparent preponderance of parallel-sided twin bands is an optical illusion, however. Many grains have more than one family of twins, and this definitely means that during growth, a grain which formed a twin on one plane at one place formed a twin on a different plane some place else.

As regards Dr. Treuting's suggestion on the constancy of number of twins, it explains the increase in width to twin bands as the grain size increases, but it still seems the number of twins per grain would be expected to increase, because presumably all those formed when the grain size was small would still be there.

It seems very probable that the variation in intensity of twinning from alloy to alloy is controlled by the surface energy of interfaces. Essentially the same argument as Dr. Treuting uses, and supporting evidence for it, has been presented very recently by R. L. Fullman.

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## Atomic Relationships in the Cubic Twinned State

by W. C. Ellis and R. G. Treuting

DISCUSSION, H. L. Burghoff presiding

D. Whittham, M. Moufflard, and P. Lacombe (*British Council Research Fellow, Laboratoire du Professor Chaudron, Vitry-sur-Seine; Ingenieur de Recherches, Laboratoire de Vitry; and Maître de Recherches, Laboratoire de Vitry, Professeur Adjoint de Metallurgie, Ecole des Mines, Paris*)—The authors' work is of great interest in bringing out the geometrical relations existing between twinned lattices, and for the notion of a coincidence superlattice developed from this.

We should like to point out that a similar idea was put forward by Friedel<sup>1</sup> in his book on the subject of lattice merohedrim "merihedrie réticulaire."—When two crystals A and B are twinned with respect to a mirror plane, there exists a common superlattice, "réseau période," which is independent of the contact surface between the two crystals. The volume V of this superlattice is a simple multiple of the volume v of the lattice of crystals A, or B, (Fig. 5). This "multiple

cell" is defined by the twin plane (pqr) and a row of atoms [hkl] normal to this plane, the base being taken as the smallest unit (two-dimensional) of this plane. Two cases must be considered. First when the multiple cell, as defined, has no atom site at its center nor at the center of its faces other than (pqr),

the twinning index is defined by  $\frac{V}{v}$ . In the second

case, when one of the two above conditions does not

apply, then the twinning index is  $\frac{V}{2v}$ .

A more intuitive definition of the twinning index would be the proportion of atoms of C<sub>2</sub> which would coincide with those of C<sub>1</sub> when the C<sub>2</sub> lattice is imagined to extend on the other side of the contact surface. In the case of cubic crystals, the twinning index



is given by the relation:

$$\Sigma = (p^2 + q^2 + r^2) \text{ if } \Sigma \text{ is odd.}$$

$$= \frac{p^2 + q^2 + r^2}{2} \text{ if } \Sigma \text{ is even.}$$

(p q r) being the mirror plane.

Thus for the face-centered cubic system with twinning on the octahedral plane (111),  $\Sigma = 3$ . Similarly for body-centered cubic twinning on (112), we have also  $\Sigma = 3$ . These results are confirmed by the atomic patterns given by the authors in which it is demonstrated that, parallel to the twinning plane, one plane in every three coincides (two in every six for the diamond lattice).

The concept of "multiple cell" developed by Friedel and analogous to the coincidence superlattice of Ellis and Treuting, though it explains the general stability of the twinned group, does not forecast the position of the boundary surface between the twins. To the metallurgist, such boundary surfaces present a rather exceptional interest in the study of boundary energy. Thus the authors bring out the fact that the (111) plane of contact for face-centered cubic twinning, and (112) for body-centered cubic twinning, corresponds with conditions of minimum distortion of the lattice, though in both cases the two lattices are symmetrical with respect to either a (111) or a (112) plane.

For our part, we have tried to extend this idea of minimum distortion in the case of boundaries between multiple twins, and the lateral interfaces noted by the author.

In an earlier paper, Ellis<sup>4</sup> presented an extremely interesting example of multiple twinning in a germanium ingot, and in the following we use a similar system of symbols. Thus if a crystal A has two first-order twins B<sub>1</sub> and B<sub>2</sub> on two different octahedral planes, then B<sub>1</sub> and B<sub>2</sub> are said to be second-order twins. Thus, we have shown that between B<sub>1</sub> and B<sub>2</sub> there exists necessarily a twin relation with mirror planes (221) and (114) and (114). Fig. 5 clearly shows this relation. In a general way, the Friedel index of a twin of order p can be determined and from it the Miller indices of possible mirror planes deduced. Thus:

| Order of Twinning | Friedel Index | Mirror Planes                                                    |
|-------------------|---------------|------------------------------------------------------------------|
| 1                 | 3             | (111) or (112) (equivalent)                                      |
| 2                 | 9             | (221) or (114) (equivalent)                                      |
| 3                 | 27            | (255) or (511) (first possibility)<br>(721) (second possibility) |

In their theoretical treatment of grain boundary energy as a function of boundary and grain orientation, Shockley and Read<sup>9</sup> have directed attention to the special interest of twinned lattices with the consequent possibility of realizing boundaries of low energy other than the twin plane (energy cusp boundaries). Such boundaries or planes of good atomic fit are the lateral twin interfaces given by the authors. The number of such possibilities is infinite but in practice the surfaces of interest are thought to be limited to planes of high atomic density. Stereographic projections for first, second, and third-order twinning enable the indices of planes which are parallel in the two lattices to be determined; and all such planes are possible lateral interfaces of the twin.

In the first place our attention was directed to the interfaces of second and third-order twins as it was believed that the particularly low energy of the (111) boundary would tend to suppress the appearance of other cusp boundaries in first-order twins. With this in mind, we attempted to interpret the crystal orientations in the micrograph of germanium given by Ellis.<sup>4</sup> The large crystal A (Fig. 6) has contacts only with twins B<sub>1</sub> and B<sub>2</sub> following the lettering, but we have assumed a third contact with B<sub>3</sub> at the top left hand

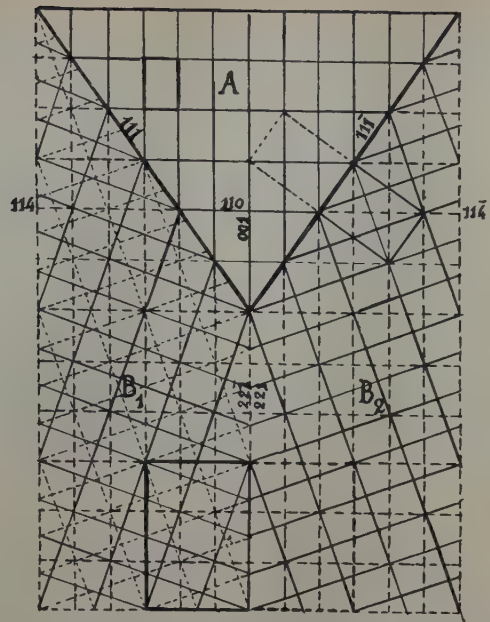


Fig. 5—Diagram showing first-order twinning between lattices A and B<sub>1</sub> (111), A and B<sub>2</sub> (111), and the resulting second-order twin B<sub>1</sub>B<sub>2</sub> with mirror planes (221) and (114).

The section shows the (110) plane parallel in all three crystals with the multiple cells of Friedel for AB<sub>2</sub> and for B<sub>1</sub>B<sub>2</sub>, in thick solid lines. The three lattices are shown by solid lines while the prolongation of a lattice is marked by dashed lines.

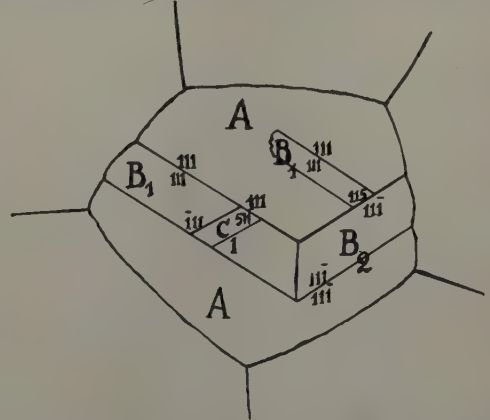


Fig. 6—Schematic drawing to show types of boundary contact between second-order twins.

B<sub>1</sub> and B<sub>2</sub> are first-order twins of A, and C<sub>1</sub> is a first-order twin of B<sub>1</sub>; B<sub>1</sub>B<sub>2</sub> and AC<sub>1</sub> are thus second-order twins.

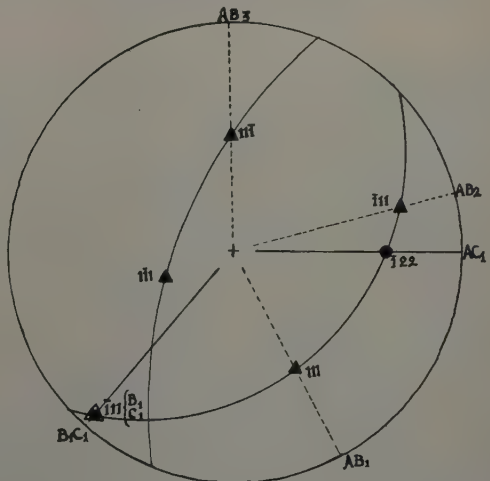


Fig. 7—Stereographic projection to fix the orientation of crystal A in the micrograph of Ellis, from the trace of (111) twin planes between AB<sub>1</sub>, AB<sub>2</sub>, and AB<sub>3</sub>.

The (122) mirror plane of the second-order twin AC<sub>1</sub> is seen to lie on the normal to the boundary between A and C<sub>1</sub>. Solid triangle —(111) poles of crystal A. Solid square in triangle—(111) twin plane for B<sub>1</sub>C<sub>1</sub>.





Fig. 8—Multiple twinning in copper sheet specimen recrystallized after a small permanent extension.

$B_1$ ,  $B_2$ , and  $B_3$  are first-order twins of  $A$ , while  $C_1$  is a first-order twin of  $B_1$  (or third-order twin of  $B_2$ ). Note the point of convergence,  $F$ , of the four crystals,  $A$ ,  $B_1$ ,  $B_2$ , and  $C_1$ . X60

side of the photograph, where the similarity of tint and parallelism of boundaries  $A-B_2$  would appear to indicate another part of crystal  $A$ . Thus in the stereogram (Fig. 7), we have plotted the (111) poles of crystal  $A$  and indicated the three twin planes. It will be remarked immediately that the twin boundary between  $B_1$   $C_1$  becomes identifiable with the (111) pole of crystal  $B_1$ ; which encouraged us to believe that the construction used was sound. The crystals  $A$  and  $C_1$  are automatically second-order twins with two possible mirror planes (221) and (114). Finally the normal to the boundary  $A-C_1$  has been traced on the stereogram and is seen to pass through the pole of the mirror plane (221) suggesting that the composition plane for this second-order twin is the mirror plane with perfect coincidence of all atoms. We would be very interested to know if our construction is in agreement with the orientations determined by X-rays, and to know whether the boundaries shown have been examined in detail.

The large number of twins found in the germanium ingot has led the authors to suggest that the diamond cubic lattice is particularly favorable for this phenomenon. We should like to point out, however, that numerous twins have also been observed in aluminum, in certain cases of semicontinuous casting.<sup>10</sup> In addition, we have found that the formation of twins of different orders is also demonstrated by the recrystallized structures of face-centered cubic metals such as copper, aluminum, and stainless steel (18/8). One such ex-

ample is shown in Fig. 8, taken from a copper sheet specimen which had been elongated 1.5 pct and then annealed at 900°C to obtain large crystals, after the method of Carpenter and Tamura.<sup>12</sup> The large crystals so obtained are not immediately evident as they are almost always subdivided into a system of multiple twins. The size of the individual twins was too small for convenient examination by the Laue method, but the problem of determining orientations was considerably simplified by forming a thin sulphide film<sup>13</sup> on the surface. As all grains having a given crystal plane parallel to the surface develop the same interference color, we preferred examination in polarized light because only those grains of the same orientation (in three dimensions) are similarly colored (see Fig. 9). Evidently for a precise determination of orientation relationships it was necessary to choose grain groups in which at least one grain had accompanying twins showing the trace of three different (111) planes.

The stereogram of Fig. 10 has been constructed in this way making use of the (111) twin boundaries between  $AB_1$ ,  $AB_2$ ,  $AB_3$ . The orientation relationships may thus be represented:

$$\begin{array}{c} B_3 \rightarrow A - B_1 - C_1 \\ \downarrow \\ B_2 \end{array}$$

with boundary contacts between the second-order twins  $B_1$   $B_2$ , the third-order twins  $C_1$   $B_2$ , as well as the remaining first-order twins. The micrograph shows a number of phenomena which are typical in the sense that they occur frequently.

1—The boundary surfaces between twin crystals of the second and third order do not coincide with the possible mirror planes. Whenever the contact is not a plane one, at the magnification used, it is of course not possible to determine the crystal surfaces involved. A number of plane surfaces have nevertheless been observed of which we mention particularly the contact (111)<sub>A</sub> (115)<sub>B</sub>, because of its frequent occurrence and as evidence of a boundary mentioned specifically by the authors, to demonstrate the exact coincidence of atoms possible on a lateral interface though applying to only one third of the atoms, due to the difference in atomic density for the two planes.

2—The surface between first-order twins is in large part the (111) twin plane but a number of other planes of contact were observed. Thus a boundary which at low magnification was apparently curved was often found to consist of series of small steps at a much higher magnification. One such example taken from a twin in aluminum is shown in Fig. 11.

3—Finally, an example is shown of four boundaries meeting in a single point. As this point of convergence was conserved after several successive polishing op-

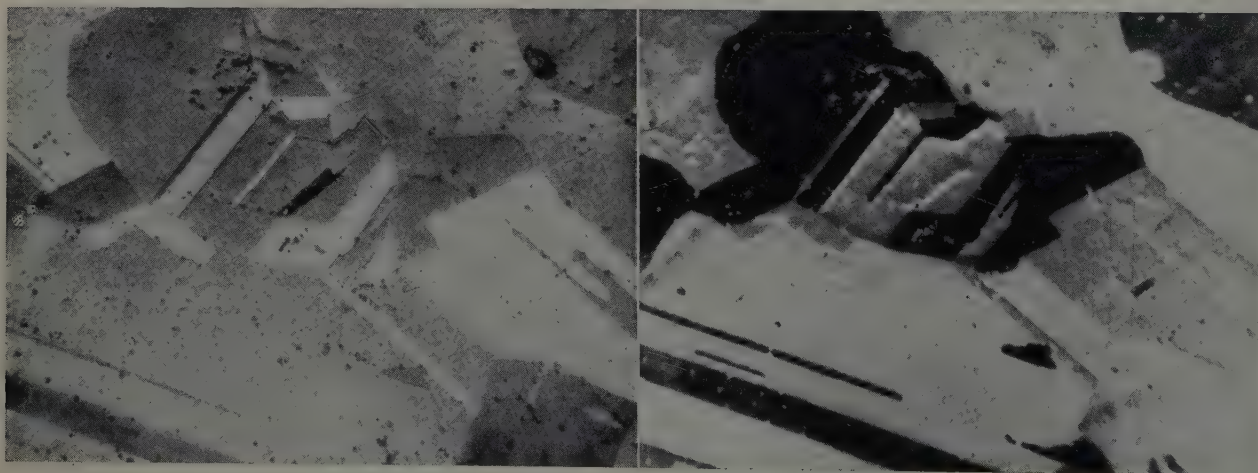


Fig. 9—Micrograph of copper carrying a thin sulphide film for recognition of grains of the same orientation by examination in polarized light between crossed nicols. X60.

Owing to the difficulty of reproducing colored photographs, Fig. 9 was replaced by two black and white photographs of the same grain group as seen in ordinary and polarized light. Difference in contrast is apparent but the wider variety of tints and color sensitivity cannot be appreciated.



erations, it is deduced that the four surfaces must meet in a row of atoms. Knowing that three of the four surfaces are in fact (111) twin planes, it becomes evident that the row of atoms corresponds to a [101] direction which is the zone axis to the three (111) planes. Such an arrangement can therefore only occur when the third-order twin between  $C_1B_2$  is of the type with mirror planes (511) — (255); and not for the alternative (721) twin.

As already noted, our observations were made on specimens which had been recrystallized and thoroughly annealed, suggesting that such structures are comparatively stable. That the boundary between first-order twins so often consists of a series of different plane junctions, which meet in an edge row of atoms, is an interesting confirmation of the theoretical forecast by Shockley and Read<sup>9</sup> that certain boundary positions produce cusps in their energy-orientation curve.

Without specifying any precise mechanism of twin formation, it seems nevertheless probable from the morphology of multiple twin groups that whereas first-order twins are generated directly from a primary crystal A, second and higher order twins are the

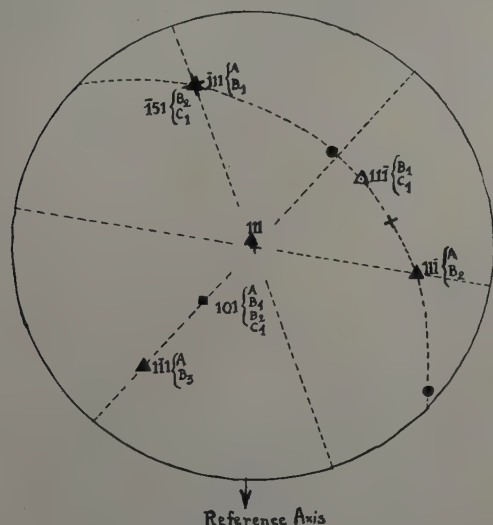


Fig. 10—Stereogram constructed from the traces of twin planes  $AB_1$ ,  $AB_2$ , and  $AB_3$  of Fig. 8.

Solid triangle—(111) poles of crystal A. Open circle in triangle—(111) twin plane of first-order twin  $B_1C_1$ . Solid circle—Mirror planes (114) and (221) of the second-order twin  $B_1B_2$ . Greek cross—Mirror planes (115) and (552) of the third-order twin  $C_1B_2$ . Solid square—direction [101] common to the four crystals, A,  $B_1B_2$ ,  $C_1$ .

incidental result of junction between two such twins  $B_1$  and  $B_2$ .

In the latter case, the junction surface may or may not have any special orientation as demonstrated by the scheme of Fig. 6. Whether such boundaries can move to some other position, representing lower energy, is not known but is now being studied. This question has already been studied in some detail by Dunn and coworkers<sup>14</sup> for the body-centered cubic system (iron-silicon).

**W. C. Ellis and R. G. Treuting** (authors' reply)—The discussion of Messrs. Whitman, Moufflard, and Lacombe is a valuable addition to the paper, particularly appreciated in that it offers experimental evidence in support of the thesis projected by the authors. We are also grateful to the discussers for making available in English so concise and illuminating a résumé of the earlier exposition of coincidence sites and multiple cell structure in twinned lattices by Friedel. This reference, we regret, was overlooked.

Professor Lacombe and his colleagues are entirely correct in their deductions of the correlations of twin relations and interface traces in the micrograph in an earlier paper<sup>4</sup> by one of the authors. X-ray evidence, not included in the earlier paper, attests to this concordance. The straight portion of the second-order junction trace, A- $C_1$ , is consistent with a {221} plane, one

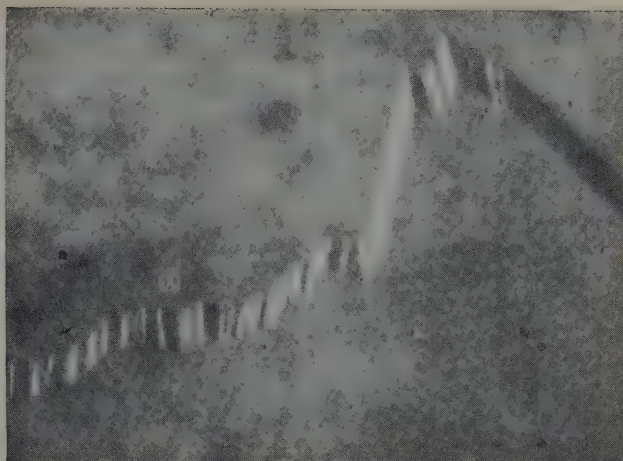


Fig. 11—Boundary between twinned crystals of aluminum, apparently curved at small magnification, but resolved into a series of steps parallel to different crystal planes.

The boundary appears thick under the oblique illumination used because the twin plane lies almost parallel to the surface. X2000.

of the mirror planes of regions A and  $C_1$ . We had been discouraged from making a point of this, however, since the A- $C_1$  junction appears curved at low magnifications over a considerable portion of its extent. The curved portion conceivably may consist of distinct crystallographic segments to be revealed only by very careful surface preparation and examination at high magnification. This is an attractive possibility; but we have not yet made such examinations.

The discussers have added a welcome reference (reference 10) to the occurrence of twins in semicontinuously cast aluminum. We do not think that this seriously weakens our suggestion that the diamond cubic structure is particularly favorable for twinning, but rather strengthens it. The aluminum ingot referred to appears to be made up in the central portion of long parallel natural grains or crystals each of which is twinned. The slice from the germanium ingot, however, consists entirely of regions in multiple twin relationships. This multiple twin relationship has more recently been confirmed throughout an entire ingot and may quite confidently be presumed general.

In the course of following the interesting deductions of Professor Lacombe and his colleagues with respect

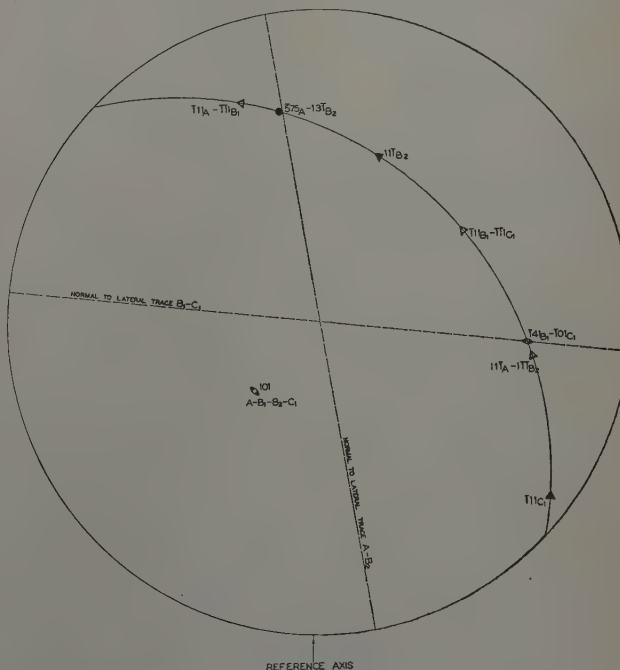


Fig. 12—Stereographic projection constructed from traces in Fig. 8 to illustrate types of coincidence at lateral twin boundaries.

to the twinned copper sheet of Fig. 8, we have reconstructed the stereographic representation of their Fig. 10 employing also normals to additional boundary traces as directly measured on the micrograph. It is evident that the rotations generating  $B_1$  and  $B_2$  from  $A$ , and  $C_1$  from  $B_1$ , can all be taken to be  $70^\circ 32'$  each about the common pole [101], which is the conserved line of intersection of four boundaries pointed out in discussion.

We first directed our attention to the boundary between the third-order twins  $B_2$ - $C_1$ , which appears fairly straight. We succeeded in ascertaining only that it coincides with neither the {115} nor the {525} mirror plane between these orientations in agreement with the findings of the discussers. This boundary could be a (111) plane of  $B_2$ , but seems to have no index pair low for both orientations.

On the other hand, the lateral boundaries between first-order twin pairs  $A$ - $B_2$  and  $B_1$ - $C_1$ , the loci of whose normals are shown in Fig. 12, are very closely consistent with, respectively, the planes (575) of  $A$  and (131) of  $B_2$ , and the planes (141) of  $B_1$  and (101) of  $C_1$ . Both these pairs, as well as the {111}::{115} type, lie in the common [101] zone, which thus seems to be experimentally indicated a favorable one for the occurrence of coherent lateral boundaries. The  $(575)_A::(131)_{B_2}$  is a lateral twin boundary also found in copper by Fullman<sup>15</sup> in his extensive examination of grain interfaces,

but this is the only pair of low-indexed planes consistent with any of the lateral twin boundaries observed by him.

The statement by the discussers that second and higher order interfaces are incidental junctures between directly generated first order and successive first orders is not to be contradicted by the evidence for copper here presented. The case for germanium may be different: here all orientations in the ingot seem interrelated through sequences of twinning. It is not inconceivable that in the diamond cubic lattice second or higher orders of twins are formed simultaneously or in direct sequence in the course of solidification.

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- <sup>14</sup> C. G. Dunn, F. W. Daniels, M. J. Bolton: *Trans. AIME* (1950) **188**, p. 368; *JOURNAL OF METALS* (February 1950).
- <sup>15</sup> R. L. Fullman: Private communication.

## Graphite-Rod Hairpin-Resistor Radiation Furnace for High Temperatures

by W. J. Kroll, W. W. Stephens, and J. P. Walsted

DISCUSSION, J. P. Nielsen presiding

**C. M. Decroly** (*University of Brussels, Belgium*)—W. J. Kroll and his collaborators are to be congratulated for the beautiful piece of work they are performing at the Bureau of Mines Experiment Station at Albany, Ore. The furnace they describe in their paper is quite interesting and the use of the hairpin graphite resistor is a very good solution of the problem of heating such a furnace. The use of that kind of resistor is not altogether new. In our researches on the thermal metallurgy of zinc carried out in collaboration with Professor O. Dony<sup>9</sup> before World War II in our laboratory, we systematically made use of such types of resistor. They were made by cutting zig-zag graphite plates of the desired thickness with allowance for an increased area at the contact with the water-cooled connections with the copper conductors.

We used them either for internal or external heating for power input up to 20 kw. One of our furnaces was heated with two resistors about 47 in. long. Providing the thickness of the graphite is sufficient, there is no special danger of breakage. The advantages of such resistors are emphasized by the authors. The increase of resistance that can be obtained is very interesting because it is possible to avoid the purchase of a special high intensity transformer. Fig. 3 shows one of the resistors we used in one of our zinc furnaces.

**W. J. Kroll** (authors' reply)—Professor Decroly's observation that the use of a slotted graphite resistor to heat electric furnaces, such as the one described by the authors, is not entirely new, is quite true. Such resistors were used some fifty years ago and the early ironing irons, proposed to housewives around the year 1906, i.e., before the arrival of nichrome resistor elements, were heated with graphite grids precisely of the form recommended later by Professor Decroly himself. Whether such resistors are made by slotting plates or tubes does

<sup>9</sup> O. Dony and C. M. Decroly: *Recherches Théoriques et Expérimentales sur la Métallurgie Thermique du Zinc*. Liège (1933).



Fig. 3—Resistor used in a zinc furnace.

not matter. The Arsem furnace is another typical example of slotting a graphite resistor. The novelty claimed does not reside in the resistor, but in its use for a specific purpose and in the solutions of technical problems concerning its application. Professor Decroly's resistors would probably not perform too well in the high temperature zirconium carbide furnace because of poor contact resulting from the use of plates and high voltage caused by the high resistance. The split rod is simpler, less sensitive, offers better contact opportunities, and has a sufficiently low voltage to prevent arcing in the slot, a very important item when considering the high temperature involved.



# Ignition Temperatures of Magnesium and Magnesium Alloys

by W. Martin Fassell, Jr., Leonard B. Gulbransen, John R. Lewis, and J. Hugh Hamilton

## DISCUSSION, J. P. Nielsen presiding

**T. E. Leontis** (*The Dow Chemical Co., Midland, Mich.*)—This paper is of particular interest to me because of my own work with F. N. Rhines on the oxidation of magnesium and magnesium alloys a few years ago. The authors are to be complimented on their development of an accurate and reproducible technique for measuring ignition temperatures and on their comprehensive study of the many variables that affect the ignition temperature of magnesium.

It is indeed gratifying to see that they have obtained a good correlation between ignition temperatures and the oxidation rates reported by us. The correlation is valid not only with composition within one alloy system but also between alloy systems; that is, alloying elements which effect the greatest increase in oxidation rate also produce the greatest decrease in ignition temperature.

There are a few points upon which I would like to comment. In attempting to correlate ignition-temperature data, one must be sure that the same definition of this quantity is used by all investigators. It does not appear to me that such is the case in the authors' comparison of their data with the theoretically calculated values of Eyring and Zvolinski. The equation derived by these investigators defines the ignition temperature,  $T_0$ , as the temperature at the gas/oxide interface, whereas the present authors use the metal temperature as the criterion for ignition. The contradiction in the effect of oxide-scale thickness on ignition temperature between the predictions of the Eyring-Zvolinski equation and the observations reported in this paper indicate that some variable has not been taken into consideration. Could that be the geometry and size of the specimen? There is a marked difference in the type of specimen used in this investigation and that used in our work which formed the basis of Eyring and Zvolinski's theoretical treatment. Another factor which plays an important role in ignition is the vapor pressure or the rate of vaporization. Combustion can safely be assumed to take place in the vapor phase by the reaction between vaporized magnesium and oxygen. Thus, a more accurate theoretical analysis may be made on the basis of the rate of vaporization which may be the controlling rate of the process.

The effect of a large number of alloying elements on the ignition temperature has been reported in this paper, but beryllium was not included. Practical experience dictates that beryllium markedly decreases the burning tendency of magnesium. I was wondering if the authors plan to study the effect of beryllium in their future work.

The authors predict that concentrations of sulphur dioxide in the furnace atmosphere greater than 5.8 pct would be expected to increase the ignition temperature to values still higher than those they measured. I would like to mention that large concentrations of sulphur dioxide markedly increase the rate of combustion of magnesium once ignition has started. Although it has been shown in the paper that the ignition temperature of magnesium in oxygen increases with increasing sulphur dioxide content up to about 1 to 2 pct, in practice relatively low-melting commercial cast alloys (AZ63A and AZ92A) are being continuously heat treated at temperatures just below the melting point in air containing 0.5 to 0.75 pct  $SO_2$ .

In regard to the change in color of the oxide scale observed on magnesium and magnesium alloys just prior to ignition, I would like to mention that in our work alloying elements were found to color the usually white magnesium oxide even though ignition did not occur. For example, the oxide formed on Mg-Al alloys

was gray, increasing in intensity with aluminum content in the alloy.

Finally, I might suggest that the authors indicate their source of the value of 0.8 g per cc for the density of  $MgO$  as it is formed on magnesium upon oxidation at elevated temperatures.

**W. M. Fassell, Jr.** (authors' reply)—The comments by Dr. Leontis are very excellent ones and I will attempt to answer them in order.

First, the problem of ignition of magnesium is a rather difficult one since many factors are involved. Concerning the comparison of the  $T_0$  in the Eyring-Zvolinski equation, eq 4, with the experimentally determined values, it will be noted that the calculated and experimental values of the ignition temperature in Table I are not self-consistent. In the case of the 1.78 pct Al-Mg alloy the calculated value is  $49^\circ C$  below the experimental value; for the 3.81 pct Al-Mg alloy,  $122^\circ C$  below the experimental value; for Mg with  $5 \times 10^{-2}$  cm film,  $19^\circ C$  above the experimental value; for Mg with  $2 \times 10^{-1}$  cm film,  $28^\circ C$  below the experimental value. Thus, if it were merely a matter of difference of location of temperature measurement the calculated ignition temperature would always be below the experimental value, the difference being due to the thermal gradient through the oxide film.

The possibility of a thermal gradient in the magnesium metal must be considered. From Carslaw and Jaeger,<sup>10</sup> it can be shown that the maximum temperature gradient that could exist between the oxide-metal interface and the center of the sample is of the order of  $0.01^\circ C$ .

The geometry and size of the specimen could certainly have some effect on the ignition temperature. The equation for ignition that has been proposed in reference 14 is of the following type containing terms to account for this and other factors:

$$\Delta H v(T) = C_p \frac{M}{A} \frac{dT}{d\tau} + J(T - T_b) + \Sigma \Delta H_L M$$

where  $\Delta H$  is the heat of reaction,  $v(T)$  is the velocity of the reaction at temperature,  $C_p$  is the heat capacity of sample,  $M$  is the mass of sample,  $A$  is the area of sample,  $\tau$  is time,  $J$  is the total coefficient of heat transfer outward from the reaction zone,  $T_b$  is the temperature of the bath or furnace, and  $\Delta H_L$  is the heat associated with any phase change involved. Prior to the instant of ignition, the vapor pressure of magnesium is of no special significance. After ignition, neither eq 4 nor the above equation is applicable. The actual combination of magnesium cannot safely be assumed to take place in the vapor phase.

While experimental data is lacking to support a hypothesis that ignition does or does not occur in the vapor phase, some observation on the pressure ignition experiments may be of interest. At high oxygen pressures, once ignition has occurred, the reaction of magnesium with oxygen approaches near explosive violence, the entire sample being consumed in probably less than 1 sec. At atmospheric pressure it usually requires 15 to 20 sec. Thus it appears that the oxygen concentration becomes the rate determining factor. Further, if burning magnesium is observed through darkened glass (Lincoln Super-Visibility Shade No. 12) the magnesium sample is very much hotter than the "smoke" and the outline of the sample is retained perfectly. No "flame" is visible above the metal.

No work was done on Mg-Be alloys. We do, however, intend to study this problem in the near future.

<sup>10</sup> H. S. Carslaw and J. C. Jaeger: *Conduction of Heat in Solids*. Oxford (1947), p. 275, eq. 2. Clarendon Press.

Concerning the AZ63A and AZ92A Mg alloys, I assume that you are giving them a solution heat treatment which normally is conducted just below the solidus temperature. Ignition in composition range of AZ62A and AZ92A occurs in oxygen between the

solidus and liquidus temperatures. Thus it is understandable that no difficulties are encountered.

The value of 0.8 g per cc for the density of MgO as it is formed on magnesium upon oxidation was calculated from reference 1, Fig. 16.

## Mechanical Properties of Stainless Steel Powder

by Arthur H. Grobe and George A. Roberts

DISCUSSION, L. A. Barera presiding

**H. H. Hausner** (*Sylvania Electric Products Inc., Bayside, N. Y.*)—I tested the 18-8 stainless steel powder described by Grobe and Roberts and the results were excellent. The powder was compacted and sintered in purified hydrogen to a very low density (approximately 20 pct and more porosity). Where the other powders show very little ductility when sintered to such a low density, the described stainless steel was surprisingly high in ductility. I would appreciate it if the authors could give us some data on a similar powder but without silicon and also data on 430 stainless steel powder.

**H. S. Kalish** (*Sylvania Electric Products Inc., Bayside, N. Y.*)—I should like to verify the excellent results obtained by Grobe and Roberts with their pre-alloyed stainless steel powder. It seems to me, however, that their data are conservative and that even better densities and higher tensile strength can be obtained with these powders by the selection of proper particle size fractions.

The accompanying data were obtained by sintering compacts pressed from the powder made by Vanadium-Alloys Steel Co. to 0.8 in. in diam about ¼ in. high in a cylindrical double action die without the use of lubricant. The compacts were sintered for 1 hr at 2370°F in hydrogen purified by passing it through a Deoxo unit (palladium catalyst) and a Lectrodryer.

Even the density obtained using the as-received (—100 mesh) compacted at 40 tsi was quite high as was the hardness. This indicates that by increasing the sintering temperature slightly above 2350°F the coining and subsequent secondary sintering operation can be avoided.

With the — 325 mesh fraction, however, very much higher density can be obtained and a high hardness.

| Powder Fraction         | Compacting Pressure, tsi | Pressed Density, g per cm <sup>3</sup> | Sintered Density, g per cm <sup>3</sup> | Hardness Rockwell, F |
|-------------------------|--------------------------|----------------------------------------|-----------------------------------------|----------------------|
| —100 mesh (As-received) | 40                       | 5.94                                   | 6.77                                    | 86.9                 |
| —270 + 325 mesh         | 40                       | 5.81                                   | 6.85                                    | 92.3                 |
| —325 mesh               | 40                       | 5.88                                   | 7.35                                    | 99.6                 |
| —100 mesh (As-received) | 60                       | 6.51                                   | 7.16                                    | 97.0                 |
| —270 + 325 mesh         | 60                       | 6.49                                   | 7.26                                    | 98.9                 |
| —325 mesh               | 60                       | 6.43                                   | 7.52                                    | 102.3                |

I have no tensile data to present, but I feel that it is not too optimistic to expect that unusually high tensile strengths and good ductility can be obtained in this sintered material on the basis of the density and hardness data.

The sintered stainless steel made by the above-described methods came out of the furnace very bright and clean. The purified hydrogen atmosphere is important in sintering stainless steel to reduce the oxide present in the powder. The result of such a sintering is good densification and good ductility of the sintered product.

**G. A. Roberts** (authors' reply)—We are greatly indebted to Messrs. Hausner and Kalish for their discussions of our paper. Their encouraging remarks are greatly appreciated and their confirmatory data will do much to add to the value of the paper. At the present time it is impossible to provide complete data on a similar stainless steel powder without silicon, but we do know that, in general, the properties are slightly inferior. Data on such a powder and on other stainless steel types are to be published in the near future.

## Rate of Sintering of Copper Under a Dead Load

by F. N. Rhines and H. S. Cannon

DISCUSSION, L. A. Barera presiding

**H. H. Hausner** (*Sylvania Electric Products Inc., Bayside, N. Y.*)—The results reported by the authors are interesting because they contribute some information on the principles of sintering and also because of a certain practical value for the manufacture of powder metallurgical parts in production. Pressed powder compacts are frequently sintered in a boat in several layers so that the lower layers are actually sintered under the weight of the upper layers and, therefore, are frequently deformed. The authors gave information on this deformation process by determining the effect of the load on the density. The experimental setup of the authors, however, has a disadvantage—that the sintering occurred in a cylindrical container so that the deformation was stopped in the direction of the diameter. The authors should have rather called this a study of hot-pressing than of sintering.

I want to call the attention of the authors and others interested in sintering under load to the experimental work described by Dawihl and Rix.<sup>1</sup> These authors sintered cylindrical compacts under a lengthwise tensional load of 0 to 25 g and found that the shrinkage in length and diameter changes considerably with the load, but that the volume shrinkage is affected very little by the load.

**H. S. Cannon** (authors' reply)—We wish to thank Dr. Hausner for calling attention to the experimental work of Dawihl and Rix. The fact that they found volume shrinkage little affected by varying tensional loads during sintering seems to support the contention that the forces due to loading are equivalent to and additive to the forces which cause densification. This contention is the basis of our comparison of sintering and creep.

<sup>1</sup> W. Dawihl and W. Rix: Effect of Tensional Forces on the Shrinkage of Metal Powder Compacts during Sintering. *Ztsch. f. Metallkunde* (1949) 40, pp. 115-119.



# Recovery of Vanadium from Titaniferous Magnetite

by Sandford S. Cole and John S. Breitenstein

The recovery of over 80 pct of the vanadium values in titaniferous magnetite from MacIntyre Development, Tahawus, N. Y., was accomplished by an oxidizing roast with  $\text{Na}_2\text{CO}_3$ - $\text{NaCl}$  addition. Process description is given for leaching of roasted ore and precipitation of  $\text{V}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  from leach liquor.

THE exploration and development of the MacIntyre orebody at Tahawus, N. Y., by the National Lead Co. provided a source of vanadium. Analyses of various composite sections of the drill cores of the MacIntyre orebody were made to establish whether or not the vanadium was constant throughout. Ten drill cores were sampled as 50 ft sections, crushed, and a portion magnetically concentrated. The head and concentrate were analyzed for total iron and vanadium. The results on the concentrates indicated that the vanadium is associated with the magnetite and maintains a close ratio to the iron content. The nominal ratio of 1:25:140 of V:TiO<sub>2</sub>:Fe was found to exist in the concentrates. Typical value for the vanadium in the magnetite both from laboratory concentration and mill production is 0.4 pct.

The recovery of vanadium from the magnetite was investigated in 1942 to 1943. The research program encompassed both laboratory and pilot-plant work on sufficient scale to provide adequate data to establish the feasibility of a full scale plant.

The recovery of vanadium from various ores has been reported in the literature and has been the subject of many patents. The literature dealing with recovery from titaniferous ore by roasting is quite limited. Roasting with alkaline sodium chloride, sodium chloride or alkaline earth chlorides, and sodium acid sulphate have been claimed in various processes as effective means.<sup>1-8</sup> The reduction of the ore, followed by acid leaching, was another method proposed.<sup>9-10</sup> The use of various pyrometallurgical processes for recovery of vanadium in the metal or in the slag has also been extensively investigated, but the results had little application to the problem.<sup>11-14</sup> The separation of vanadium values from subsequent leach liquors and vanadium-bearing solution has been the subject of a considerable number of papers and patents. The most practical is by hydrolysis at a pH of 2 to 3 by acidifying a slightly

alkaline solution. Data on solubility of  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_4$  in water and in dilute sulphuric acid indicated a solubility of 10 g per liter in water.<sup>16</sup>

## Laboratory Results

**Magnetite Analysis:** Adequate stock of magnetite was provided so that the laboratory and pilot-plant operation was on ore representative of the mill production. The ore was analyzed chemically and examined by petrographic methods to ascertain whether the vanadium was present in combined state or as an interstitial component between grain boundaries. No evidence was obtained which would indicate that the vanadium was in a free state as coulsonite.<sup>15</sup> The analysis of the ore was as follows: Fe<sub>2</sub>O<sub>3</sub>, 47.4 pct; FeO, 29.1; TiO<sub>2</sub>, 10.1; V, 0.40; and Cr, 0.2.

The screen analysis of the ore on the as-received basis was: -20 +30 mesh, 28.8 pct; -30 +40, 18.9; -40 +50, 9.7; -50 +60, 15.1; -60 +100, 5.9; -100 +200, 11.2; -200 +325, 3.7; and -325, 7.2.

**Roasting Conditions:** The prior practice indicated that a chloridizing roast with or without an alkaline salt had been effective on other titaniferous magnetites. On this basis roasts with additions of sodium chloride, sodium carbonate and mixtures thereof were investigated varying the roasting temperature between 800° and 1100°C. Since the ore had shown no segregation or concentration of vanadium, the influence of particle size on the freeing of vanadium by the reagents during roasting was determined. The initial work was on silica trays in an electric resistance furnace with occasional rapping of the charge. Subsequently, the roasting was carried out in a small Herreshoff furnace to establish the influence of products of combustion on the recovery of the vanadium.

The laboratory tests showed that this ore required an alkaline chloridizing roast, in conjunction with a reduction in particle size to less than 200 mesh. When roasted in air at 900°C with 5 pct NaCl and 10 pct Na<sub>2</sub>CO<sub>3</sub>, over 80 pct recovery of the vanadium was attained as a water-soluble salt. The presence of alkaline earth elements gave detrimental effects and care had to be exercised to avoid any contamination of the ore or roast product by such materials.

The solubilization of vanadium under the various conditions is given in a series of curves in Figs. 1 to

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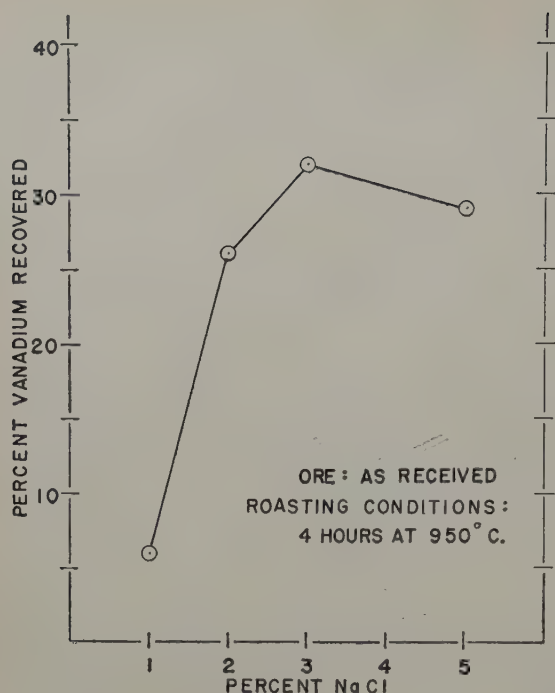


Fig. 1—Effect of roasting as-received ore with NaCl at 950°C.

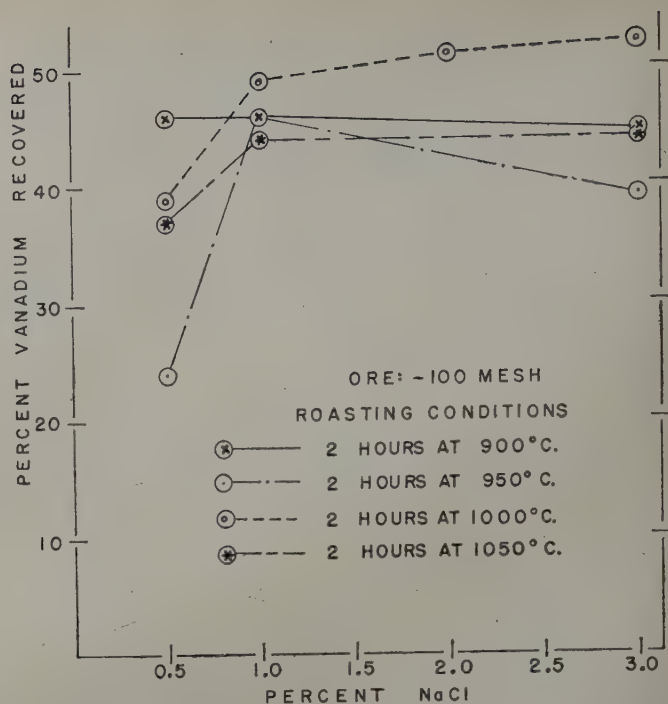


Fig. 2—Effect of roasting ground ore with NaCl at various temperatures.

6. The influence of the several factors is quite apparent. The general conditions for processing the ore as determined by the roasts are shown in Table I.

**Leaching Conditions:** Leaching of the roasted ore was varied using percolation and countercurrent washing. The retention of solution on the ore was not found to be critical since the vanadium-bearing salts were on the surface of the ore particle. The use of countercurrent stages for leaching was desirable since the concentration of vanadium could be increased to 10 to 20 g per liter, thus reducing the volume of liquor in process. Four to five stages of leaching removed 98 to 100 pct of the soluble vanadium. The increase in vanadium content of the leach liquor is shown in Fig. 7 when the leaching was carried out for six stages. Crushing the consolidated lumps to -10 mesh and avoiding forming of -100 mesh material yielded the optimum product. Large amounts of -100 mesh material gave a slow rate of filtration. The rate of diffusion of the leach liquor into lumps coarser than 10 mesh retarded the rapid removal of the soluble vanadium. The use of water at 80°C was found to give a slight improvement, especially in conjunction with suppression of aluminum salts.

#### Recovery of Vanadium and Other Values

The leach liquor from a chloridizing alkaline roast contained the vanadium as a sodium vanadate, sodium chromate, sodium aluminate, sodium chloride, sodium carbonate, and sodium sulphate. The cyclic recovery of sodium values was desirable and elimination of aluminum salts was necessary. The suppression of aluminum during leaching by a carbon dioxide atmosphere was found to be the most satisfactory.

Precipitation of vanadium as a calcium vanadate complex in presence of  $\text{CaCl}_2$  and  $\text{Ca(OH)}_2$  was satisfactory for leach liquors derived from salt roast or when the liquors were low in sulphur values. The optimum ratio by weight of reagents to vanadium was  $2\text{Ca(OH)}_2:\text{V}$  and  $1-1.4\text{CaCl}_2:2\text{V}$  with-

out altering the pH of the leach liquor. This procedure had considerable merit when working with solutions having vanadium at low concentrations of the order of 0.5 to 5 g per liter.

Hydrolysis of vanadium from the leach liquor was based upon the use of nucleating conditions and adjusting the pH to  $2.5 \pm 0.2$ .<sup>18, 19</sup> The solution was acidified with sulphuric acid at room temperature and up to 80°C. The temperature was held at 95°C for 1 hr and then the solution was boiled for an additional hour. The acidification was done without agitation over a 10 min period. The slow formation of nuclei of  $\text{V}_2\text{O}_5$  occurred and on subsequent heating and agitation large nodules or flocs of 1/16 to 1/4 in. diam formed. No appreciable formation of  $\text{V}_2\text{O}_5$  occurred below 85°C. This practice avoided the adherence of vanadium oxide to the side walls of the vessel and the product was easily filtered and washed. The removal of vanadium was over 99 pct.

The filtrate was reduced with  $\text{SO}_2$  and the solution adjusted with  $\text{Na}_2\text{CO}_3$  to a pH of 7.0, thereby hydrolyzing chromium as  $\text{Cr(OH)}_3$ . The filtrate from this step contained only sodium chloride and sodium sulphate which was readily crystallized and separated in pure state in accordance with published data.<sup>20</sup> The sodium chloride liquor containing some sodium sulphate could be returned to the process

Table I. Conditions for Processing Ores

|                         |                                 | Mesh                      | Pct                         |
|-------------------------|---------------------------------|---------------------------|-----------------------------|
| Ore Grind               |                                 | — 80 + 100                | 0.0                         |
|                         |                                 | — 100 + 200               | 1.0                         |
|                         |                                 | — 200 + 325               | 22.0                        |
|                         |                                 | — 325                     | 77.0                        |
|                         |                                 |                           |                             |
|                         |                                 | Range                     | Optimum, Pct                |
| Reagents                | NaCl                            | 3 pct min.<br>6 pct max.  | 5                           |
|                         | Na <sub>2</sub> CO <sub>3</sub> | 6 pct min.<br>12 pct max. | 10                          |
| Temperature             |                                 | 875°-925°C                |                             |
| Atmosphere              |                                 | Oxidizing                 | 2.8-20.8 pct O <sub>2</sub> |
| Vanadium solubilization |                                 | 75-85 pct                 |                             |



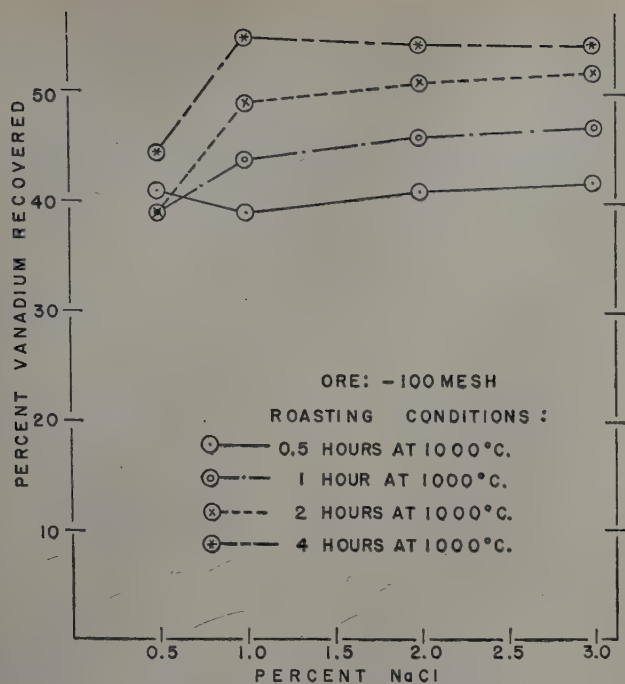


Fig. 3—Effect of roasting ground ore with NaCl at 1000°C.

without adversely affecting the vanadium recovery since it contained only these compounds. The new salt makeup was 60 pct of the total requirement.

#### Pilot-Plant Operation

Based on laboratory results and procedures, process flowsheets were devised so as to adapt the existing pilot-plant equipment to the problem. In several instances improvisation was necessary and conditions indicated by laboratory practice were not met fully. This was particularly true in the case of leaching. Laboratory tests had indicated fast filtering equipment, but none was available so barrels were substituted and the solution transferred from one stage to the next. The roasting was done in a 3x30 ft rotary kiln, fired with Bunker "C" oil. The

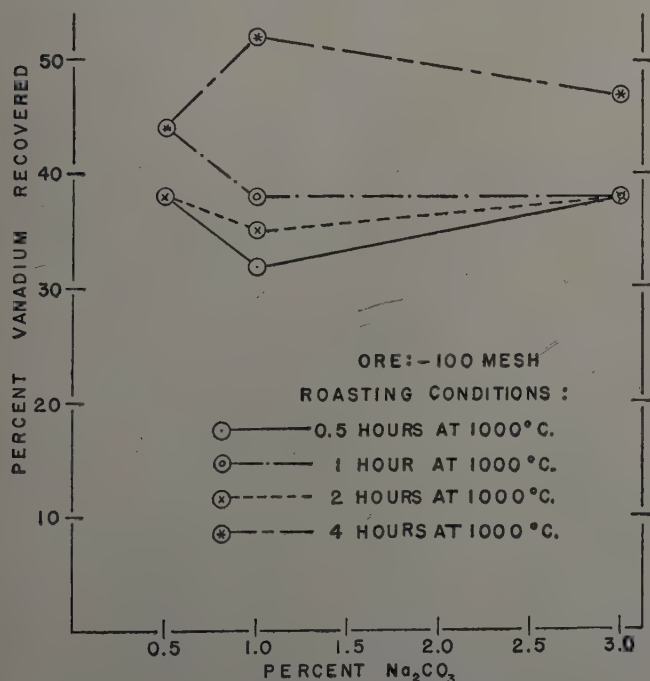


Fig. 5—Effect of roasting ground ore with  $\text{Na}_2\text{CO}_3$  at 1000°C.

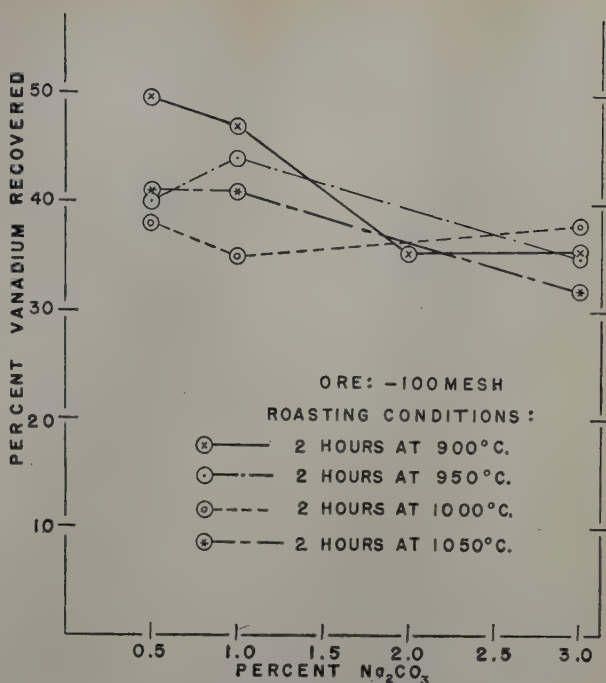


Fig. 4—Effect of roasting ground ore with  $\text{Na}_2\text{CO}_3$  at various temperatures.

processing of roasted ore and leach liquor was on a scale comparable to a half ton of feed ore per 6 hr.

The flowsheet for the recovery of vanadium from the MacIntyre magnetite utilizing  $\text{NaCl-Na}_2\text{CO}_3$  mixtures for the pilot-plant operation is given in Fig. 8. The specific conditions for each stage of the process are discussed in separate sections.

**Ore Grinding and Blending:** A small Raymond mill capable of grinding 500 to 600 lb per hr was used to prepare a feed for the rotary kiln which was comparable with ball mill ground ore. The differences in screen size were less than 2 pct of the product used for laboratory roasts.

The blending of the reagents with the ore was accomplished with a flight mixer using sufficient

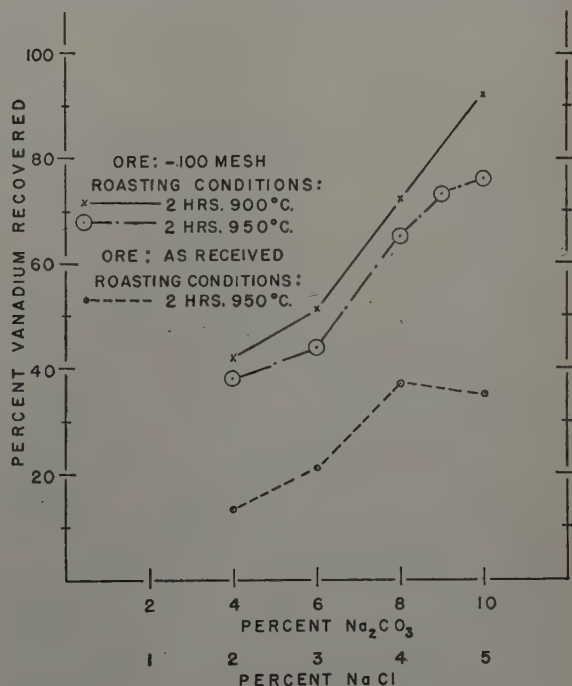
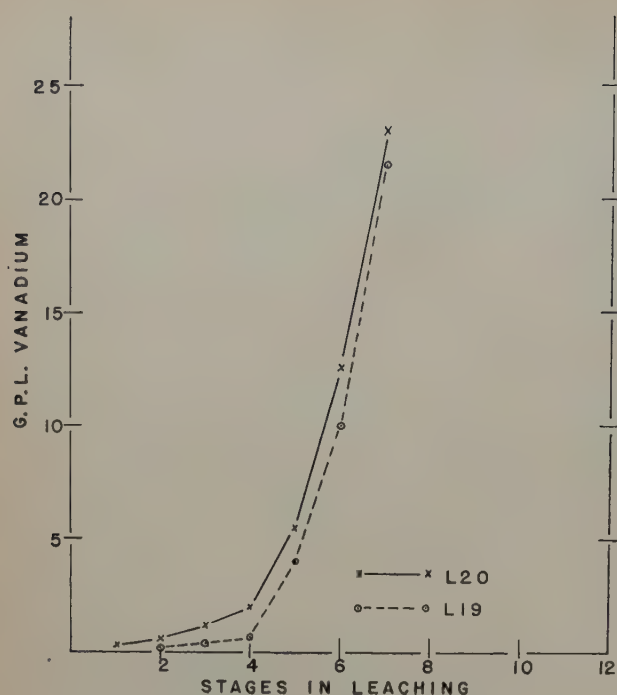


Fig. 6—Effect of roasting ground ore with  $\text{Na}_2\text{CO}_3\text{-NaCl}$  mixtures at 900° and 950°C.



water to prevent dust losses. This gave an even distribution of reagents through the ore. The mixture was then blended with water to produce a mass having 12 to 16 pct moisture. This served a dual purpose, since the reagents would be in better contact with the ore and the charge would form as balls or lumps in the kiln. The formation of lumps reduced the loss of sodium chloride during the roasting operation.

*Roasting Operation:* A bed of ore of 3 to 10 in. was maintained in the kiln which had 24 in. ID. The kiln temperatures were varied to determine what the optimum would be for pilot-plant as compared with laboratory scale. The results indicate 910° to 920°C with 1 to 2 hr retention time at that temperature. The lumps which formed about 90 pct of the discharge gave better recovery of vanadium. Table II shows the differences in retention time, temperature, and conditions of discharge.

The data obtained indicated that the general specification for kiln conditions would be as follows:

|                |                                    |
|----------------|------------------------------------|
| Temperature    | 910°-930° ± 10°C                   |
| Retention time | 45-75 min                          |
| Bed thickness  | 6 in. minimum<br>12-24 in. maximum |
| Stack gas      | 2-7 pct O <sub>2</sub>             |
| Type of feed   | Nodules ½-3 in. diam               |
| Feed bulk      | 120-130 lb per cu ft               |

In order to determine what may have contributed to the differences in recovery of vanadium from the lumps vs. fines, a complete analysis was made from

Table II. Results of Roasting

| Retention Time, Hr | Temperature, °C | Vanadium Recovery, Pct |       |
|--------------------|-----------------|------------------------|-------|
|                    |                 | Lumps                  | Fines |
| 0.5                | 910             | 73                     | 48    |
| 1.0                | 910             | 94                     | 58    |
| 1.0                | 940             | 83                     | 67    |
| 2.0                | 910             | 77                     | 80    |
| 2.0                | 920             | 89                     | 66    |
| 2.0                | 950             | 89                     | 58    |

one 24-hr operation and partial analysis of several other shorter periods. The only difference observed was in the soluble NaCl content which was considerably lower in the fines, of the order of 0.9 to 1.0 pct while lumps gave 1.4 to 1.8 pct.

Analyses on dry basis of a typical composite before and after leaching of the furnace discharge are given in Table III.

Table III. Analyses of Typical Composite of Leach

|                                | Unleached, Pct | Leached, Pct |
|--------------------------------|----------------|--------------|
| TiO <sub>2</sub>               | 8.9            | 9.1          |
| Fe <sub>2</sub> O <sub>3</sub> | 69.5           | 73.4         |
| FeO                            | 1.0            | 1.0          |
| V                              | 0.36           | 0.08         |
| SiO <sub>2</sub>               | 3.88           | 3.98         |
| Al <sub>2</sub> O <sub>3</sub> | 4.87           | 6.14         |
| CaO                            | 0.82           | 0.92         |
| MgO                            | 1.10           | 1.2          |
| Na <sub>2</sub> O              | 6.53           | 3.52         |
| NaCl                           | 2.14           | 0.12         |
| Cr <sub>2</sub> O <sub>3</sub> | 0.34           | 0.15         |
| MnO                            | 0.29           | 0.28         |
| S                              | 0.22           | 0.036        |
|                                | <hr/> 99.21    | <hr/> 99.93  |

*Leaching Roasted Ore:* The lumps were crushed to pass a 6 mesh screen and 500 lb placed in wooden barrels equipped with drainage spouts. The initial water started through the leaching cycle was 80 gal per ton roasted ore with 34 gal per ton ore being recovered from the cycle due to porosity of the lumps and retention on the ore. The final liquor averaged 17 g per liter vanadium. Comparison of laboratory leaching efficiency with that of the pilot plant gave equivalent recovery of vanadium. Results of comparison of leaching recovery with first

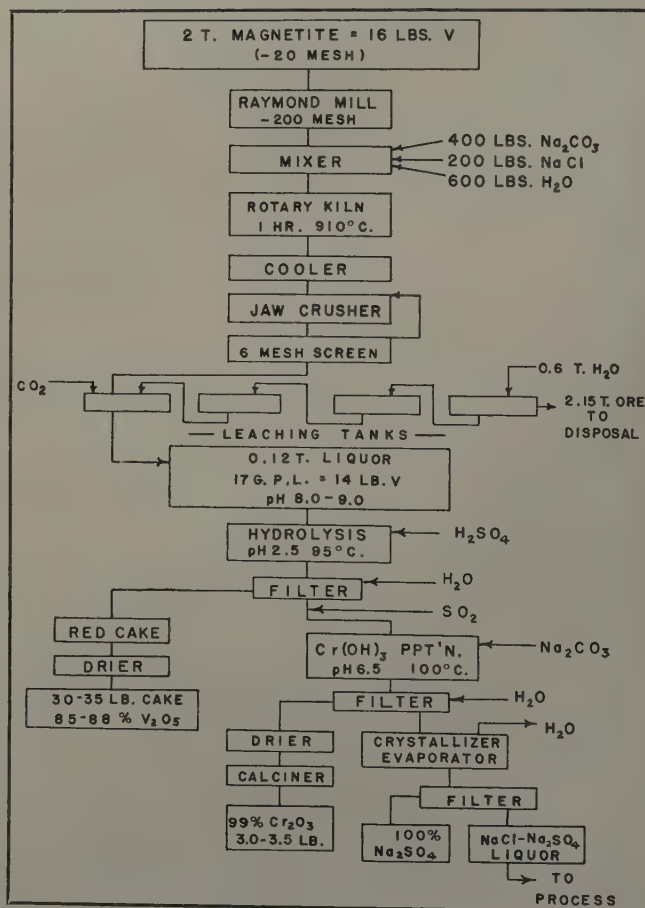


Fig. 8—Flowsheet for pilot-plant process.



and last stage showed 99.0 pct efficiency. Data on the leaching operation are as follows:

#### Comparison of First and Last Stages

|                                  |           |
|----------------------------------|-----------|
| Vanadium in first stage liquor   | 20.458 lb |
| Vanadium in last stage liquor    | 0.444     |
| Vanadium in solution held by ore | 0.20      |
| Vanadium lost in solution on ore | 0.98 pct  |

#### Conditions for Leaching

|                                                     |         |
|-----------------------------------------------------|---------|
| Ratio ore/water                                     | 3.3:1   |
| Ratio ore/liquor                                    | 15:1    |
| Stages of leaching                                  | 4-5     |
| pH leach liquor after CO <sub>2</sub> acidification | 8.8-9.2 |

#### Analysis of Leach Liquor

|                                 |                     |
|---------------------------------|---------------------|
| Specific gravity                | 1.25-1.28 at 25°C   |
| pH                              | 8.8-9.0             |
| V                               | 16-20 g per liter   |
| Al <sub>2</sub> O <sub>3</sub>  | 0-0.2 g per liter   |
| Cr                              | 2-4 g per liter     |
| Na <sub>2</sub> SO <sub>4</sub> | 120-140 g per liter |
| NaCl                            | 75-120 g per liter  |
| Temperature of leaching         | 60-80°C             |
| Ore size, -4 mesh               | 100 pct             |
| -100 mesh                       | <10 pct             |
| Retention time, first stage     | 20 min              |
| balance                         | 1-5 min             |
| Moisture, leached residue       | 14-18 pct           |

**Recovery of Metal and Salt Values from Leach Liquor:** A series of pilot-plant precipitations were made using composited lots of leach liquor. Analysis of the filtrates after each stage of vanadium and chromium removal showed over 99 pct effective removal.

Optimum conditions for recovery of the metal values based upon pilot-plant runs were found to be as follows:

#### V<sub>2</sub>O<sub>5</sub> Precipitation

|                                                  |                                               |
|--------------------------------------------------|-----------------------------------------------|
| H <sub>2</sub> SO <sub>4</sub> concentration     | 66 pct                                        |
| Temperature of solution                          | 60°-90°C                                      |
| pH after acid addition                           | 2.5-2.75                                      |
| Period for acid addition                         | >20 min                                       |
| Agitation arrested                               | >40 min (including acid addition time)        |
| Temperature for precipitation                    | 95°-100°C                                     |
| Rate of temperature rise                         | 12°C per hr                                   |
| Time at 95°-100°C                                | 1-2 hr                                        |
| Wash water for V <sub>2</sub> O <sub>5</sub>     | Volume equal to starting liquor at pH 2.5-3.0 |
| Floc volume                                      | 15-25 pct                                     |
| Filtration rate of V <sub>2</sub> O <sub>5</sub> | 5.4 g per sq cm per hr                        |
| Solids in cake                                   | 16.5 pct                                      |
| Bulk volume                                      |                                               |
| Wet filter cake                                  | 22.0 lb per cu ft                             |
| Dry filter cake                                  | 10.9 lb per cu ft                             |
| Fused cake                                       | 180 lb per cu ft                              |
| Melting point                                    | 630°-650°C                                    |

#### Analysis of V<sub>2</sub>O<sub>5</sub> Cake

|                                         |
|-----------------------------------------|
| 85-88 pct V <sub>2</sub> O <sub>5</sub> |
| 5-8 pct Na <sub>2</sub> O               |
| 5-7 pct loss on ignition                |

#### Cr<sub>2</sub>O<sub>3</sub> Precipitation

|                                                              |                                       |
|--------------------------------------------------------------|---------------------------------------|
| SO <sub>2</sub> per kg Cr                                    | 3                                     |
| Na <sub>2</sub> CO <sub>3</sub> per kg Cr                    | 4                                     |
| Temperature for reduction                                    | 60°-90°C                              |
| pH after Na <sub>2</sub> CO <sub>3</sub> addition            | 6.5-7.0                               |
| Temperature for Cr <sub>2</sub> O <sub>3</sub> precipitation | 70°-100°C                             |
| Rate of temperature rise                                     | Not critical                          |
| Time at 95°-100°C                                            | 1-3 hr                                |
| Wash water for Cr <sub>2</sub> O <sub>3</sub>                | ¼-½ volume of filtrate                |
| Floc volume                                                  | 15 pct                                |
| Filtration rate for Cr <sub>2</sub> O <sub>3</sub>           | 0.13 g per sq cm per hr               |
| Solids in cake                                               | 21.2 pct                              |
| Analysis of calcine                                          | 99 pct Cr <sub>2</sub> O <sub>3</sub> |

#### Filtrate from Cr<sub>2</sub>O<sub>3</sub> Precipitation

The filtrate available for sodium sulphate recovery had the following typical analysis from a 15 g per liter vanadium starting solution:

|                                 |                   |
|---------------------------------|-------------------|
| Volume increase                 | 15 pct            |
| pH                              | 6.5               |
| Na <sub>2</sub> SO <sub>4</sub> | 200 g per liter   |
| NaCl                            | 65 g per liter    |
| Cr                              | <0.01 g per liter |
| Specific gravity                | 1.2               |

Since this liquor could be concentrated and pure Na<sub>2</sub>SO<sub>4</sub> crystallized in a standard unit, it was not considered necessary to follow out this step.

#### Summary

A process developed in the laboratory and carried through the pilot-plant for the recovery of vanadium values from MacIntyre magnetite containing 10 pct TiO<sub>2</sub> and 0.4 pct V has been described. Grinding the ore to pass 200 mesh screen is required. The addition of 3 to 5 pct NaCl and 6 to 10 pct Na<sub>2</sub>CO<sub>3</sub> is made and roasting is under oxidizing conditions at 910° to 930°C. The effective release in soluble form of 75 to 90 pct of the vanadium contained and 50 pct chromium was accomplished by this roast.

The leaching of the roaster discharge in the presence of stack gases fixed the aluminum values in the leach cake. Conditions for precipitation of a fast filtering vanadium oxide by use of nuclei at a pH of 2.5 were established. The precipitation of chromium hydroxide after reduction of the solution with SO<sub>2</sub> at a pH of 6.5 to 7.0 yielded a sodium sulphate-sodium chloride liquor from which pure sodium sulphate was crystallized and the sodium chloride brine was returned to process. Recovery of vanadium and chromium values from the solutions was over 99 pct effective.

#### Acknowledgments

The authors wish to acknowledge the assistance given during the laboratory and pilot-plant phases by R. L. Holiday, W. F. Meister, C. H. North, and L. W. Rowe, Research Chemists of the Research Dept., and advice of J. L. Turner, Technical Director (deceased) and R. Dahlstrom, Technical Director, Titanium Div., National Lead Co.

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# Low Grade Bauxites and Clays as Potential Aluminum Resources

by K. K. Kershner, C. W. Funk, and W. A. Calhoun

Future resources of aluminum may require the utilization of low grade ores to provide a more permanent protection for the nation. Aluminum minerals such as clay, shale, and high iron laterites may become important sources. An evaluation of reserves is given. New laboratory results are reported on the Vereinigte desilication process.

THIS report on future resources of aluminum metal emphasizes the necessity for investigating utilization of low grade potential ores to provide more permanent protection for the nation. Partial or complete interruption of the importation of high grade aluminum ores must be given consideration. Ultimately, aluminum minerals such as clay, shale, and high iron laterites may become the principal sources of aluminum. The development of extractive processes for treating these low grade materials is a step in long-range national preparedness that should receive more attention. In formulating such processes, the application of beneficiation methods for the purpose of classifying the several types of minerals before subjecting each type to the more expensive extractive procedures should be considered, and a careful survey of the basic factors of power sources, transportation facilities, and sources of raw material should be made.

## Domestic Bauxite Resources

Of the domestic supply of current, treatable-grade bauxite, 95 pct comes from Arkansas. The present reserve of Arkansas bauxite suitable for metal production, including abrasive-grade, Bayer-grade, and modified Bayer-grade ores, is 34,000,000 tons. The total reserve of bauxite of all grades is approximately 75,000,000 tons. Reserves are estimated on a mined and dried basis. Data available to the Bureau of Mines in 1948 to 1949 were used in preparing Table I, which shows a breakdown by grades of bauxite for about a half of the reserves of the state.

The modified Bayer ore, 10,555,500 long dry tons, is based on a cutoff of 8 to 15 pct silica. The sub-

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Table I. Arkansas Bauxite Reserves in Deposits for which Data Were Made Available to Bureau of Mines as of Dec. 31, 1948

| Grade          | Wet Long Tons<br>in Place | Mined Dry<br>Long Tons |
|----------------|---------------------------|------------------------|
| Abrasive       | 2,863,500                 | 1,634,200              |
| Bayer          | 9,653,500                 | 5,422,000              |
| Modified Bayer | 18,497,900                | 10,555,500             |
| Subtotals      | 31,014,900                | 17,611,700             |
| Marginal metal | 7,823,300                 | 4,347,000              |
| High iron      | 8,334,300                 | 4,580,100              |
| Chemical       | 1,829,600                 | 1,145,000              |
| Submarginal    | 17,777,500                | 10,074,700             |
| Grand total    | 66,779,600                | 37,758,500             |

marginal 10,074,700 long dry tons is assumed to contain more than 40 pct gibbsite, more than 15 pct silica, and less than 32 pct available alumina. A considerable amount of this low grade material was consumed in 1949 and 1950.

Additional tonnages of bauxitic and kaolinitic clays are indicated by the Bureau of Mines drilling project.<sup>1</sup> Applying a 50 pct factor to arrive at long tons mined and dried, the results of this project are approximately 31,500,000 tons kaolinitic clay at +35 pct  $\text{Al}_2\text{O}_3$  and 11,800,000 tons kaolinitic clay at 20 to 35 pct  $\text{Al}_2\text{O}_3$ .

Total reserves of kaolinitic clays are probably quite extensive—several times the reserves shown in the Bureau's work. Total reserves of bauxitic and high iron clays from the drilling program and previously established figures are 63,980,000 tons.

The mineral dressing methods,<sup>2</sup> the lime-sinter process,<sup>3</sup> the lime-sinter modification of the Pederson process,<sup>4</sup> the lime-soda sinter process,<sup>5-8</sup> and the Alcoa combination process<sup>9, 10</sup> have been described in the literature and will not be elaborated upon here. The less familiar Vereinigte Aluminium-Werke process used by the Germans during World War II may require some amplification. It was used to beneficiate boehmite ores containing 12 to 18 pct silica for a feed to the European Bayer process. Ore was



Table II. Desilication of Kaolinite

| Tempera-<br>ture, °C | Time,<br>Hr | Analysis of<br>Calcine, Pct |                                |                  | Desilication<br>Residue, Pct |                                | Percent of Total Silica<br>and Alumina |                                |                   |                                | Percent<br>Available<br>Alumina,<br>Desilication<br>Residue |
|----------------------|-------------|-----------------------------|--------------------------------|------------------|------------------------------|--------------------------------|----------------------------------------|--------------------------------|-------------------|--------------------------------|-------------------------------------------------------------|
|                      |             |                             |                                |                  |                              |                                | Desilication<br>Residue                |                                | Leach<br>Solution |                                |                                                             |
|                      |             | SiO <sub>2</sub>            | Al <sub>2</sub> O <sub>3</sub> | Ignition<br>Loss | SiO <sub>2</sub>             | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub>                       | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub>  | Al <sub>2</sub> O <sub>3</sub> |                                                             |
| 700                  | 4           | 49                          | 43                             | 0.8              | 35                           | 29                             | 75                                     | 72                             | 25                | 28                             | 0.1                                                         |
| 900                  | 4           | 49                          | 44                             | 0.3              | 36                           | 42                             | 70                                     | 83                             | 30                | 17                             | 0.1                                                         |
| 950                  | 4           | 50                          | 44                             | 0.1              | 13                           | 65                             | 15                                     | 90                             | 85                | 10                             | 29.0                                                        |
| 1000                 | 4           | 51                          | 44                             |                  | 12                           | 68                             | 15                                     | 91                             | 85                | 9                              | 30.0                                                        |

reported to be calcined at 900° to 1000°C (1652° to 1832°F) to decompose kaolin to amorphous silica and alumina. The calcine was crushed to 15 mm to be suitable for percolation and was leached with a recycled 10 pct sodium hydroxide solution at 90° to 95°C (194° to 203°F) to dissolve the silica. As much as 80 pct of the silica was extracted, and as little as 2 pct of the alumina was lost. Soda was regenerated by adding lime and precipitating dicalcium silicate. The desilicated residue was treated by the European Bayer process in the same reactor.<sup>11, 12</sup>

#### Bureau of Mines Research Work—1950

Preliminary laboratory tests on the percolation leaching of silica from bauxites by the Vereinigte process<sup>11</sup> were reported by Skow and Conley,<sup>12</sup> of the College Park laboratories. Approximately 65 to 80 pct of the silica and 8 to 11 pct of the alumina were removed from bauxites containing 11.9 to 22.2 pct silica.

This desilication process is being investigated at the Rolla, Mo., and Bauxite, Ark., laboratories of the Bureau of Mines. As the silica content of low grade bauxites and clay is largely in the form of hydrous aluminum silicates, the preliminary experiments have dealt with kaolinite and halloysite.

Differential thermal analysis curves made on samples of these materials showed endothermic and exothermic peaks at 595° and 596°C (1103° and 1105°F) and 965° and 969°C (1769° and 1776°F), respectively. These two peaks correspond to the loss of water of hydration<sup>13, 14</sup> and to a transitional or transformation reaction.<sup>15, 16</sup> The two samples contained 42 and 45 pct silica and 37 and 38 pct alumina, respectively.

The samples were dry-ground in a pebble mill to -100 mesh and calcined at different temperatures

within a range of 400° to 1000°C (752° to 1832°F) for 2 and 4 hr periods. The calcines were agitated with 10 pct sodium hydroxide at 90° to 95°C (194° to 203°F) for 1 hr.

The distribution of silica and alumina in leach solutions and residues is summarized in Tables II and III. The available alumina, which is the quantity of the desilicated residue dissolved by pressure digestion with 10 pct caustic at 148°C for 10 min, and analyses of calcines also are given. The data are average values obtained from several tests.

These tables indicate that calcination above 900°C (1652°F) is required to extract an appreciable amount of silica. Below 900°C (1652°F) the silica extraction is less than 30 pct of the original content; simultaneously, approximately the same percentage of alumina is dissolved, part of which might be recovered by re-treating the leach solution. The amount of available alumina in the desilicated residues is substantially zero.

Calcination at 950°C (1742°F) affects a marked change in the percentage of soluble silica and alumina in the 10 pct caustic. It will be noted that 74 to 85 pct of the original silica is removed from calcines prepared at 950° and 1000°C (1742° and 1832°F) with the simultaneous solution of approximately 10 pct of the total alumina. In a cyclic process, a portion of this dissolved alumina would be returned as sodium aluminate with the sodium hydroxide liquor obtained from the causticization with lime to remove silica. The data also show a silica content of 12 pct in the kaolinite leach residues, as compared to 20 pct in those from the halloysite. The Vereinigte process shows reductions in silica content of 75 to 82 pct accompanied by alumina removals of 1 to 2 pct, and large-scale tower desilications produced desilicated material containing approximately

Table III. Desilication of Halloysite

| Temperature, °C |    | Time, Hr |    | Analysis of Calcine, Pct |                                |               | Desilication Residue, Pct |                                |                  | Percent of Total Silica and Alumina |                  |                                |  | Percent Available Alumina, Desilication Residue |
|-----------------|----|----------|----|--------------------------|--------------------------------|---------------|---------------------------|--------------------------------|------------------|-------------------------------------|------------------|--------------------------------|--|-------------------------------------------------|
|                 |    |          |    |                          |                                |               |                           |                                |                  | Desilication Residue                |                  | Leach Solution                 |  |                                                 |
|                 |    |          |    | SiO <sub>2</sub>         | Al <sub>2</sub> O <sub>3</sub> | Ignition Loss | SiO <sub>2</sub>          | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub>      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> |  |                                                 |
| 700             | 2  | 50       | 43 | 0.9                      | 38                             | 31            | 77                        | 71                             | 23               | 29                                  | 0.2              |                                |  |                                                 |
| 700             | 4  | 50       | 43 | 0.6                      | 38                             | 31            | 77                        | 71                             | 23               | 29                                  | 0.8              |                                |  |                                                 |
| 900             | 2  | 51       | 43 | 0.6                      | 40                             | 30            | 79                        | 69                             | 21               | 31                                  | 0.6              |                                |  |                                                 |
| 900             | 4  |          |    |                          | 39                             | 29            | 70                        | 69                             | 30               | 31                                  | 0.3              |                                |  |                                                 |
| 950             | 2  | 51       | 44 | 0.5                      | 24                             | 55            | 33                        | 87                             | 67               | 13                                  | 26.0             |                                |  |                                                 |
| 950             | 4  | 52       | 45 | 0.4                      | 21                             | 61            | 26                        | 87                             | 74               | 13                                  | 30.2             |                                |  |                                                 |
| 950             | 5½ | 52       | 45 | 0.4                      | 23                             | 58            | 30                        | 90                             | 70               | 10                                  |                  |                                |  |                                                 |
| 970             | 5½ |          |    |                          | 20                             | 64            | 23                        | 89                             | 77               | 11                                  | 28.7             |                                |  |                                                 |
| 990             | 5½ |          |    |                          | 20                             | 64            | 22                        | 90                             | 78               | 10                                  | 27.2             |                                |  |                                                 |
| 1000            | 2  | 51       | 44 | 0.4                      | 22                             | 59            | 27                        | 88                             | 73               | 12                                  | 28.0             |                                |  |                                                 |
| 1000            | 4  | 52       | 45 |                          | 21                             | 61            | 26                        | 88                             | 73               | 12                                  | 25.8             |                                |  |                                                 |

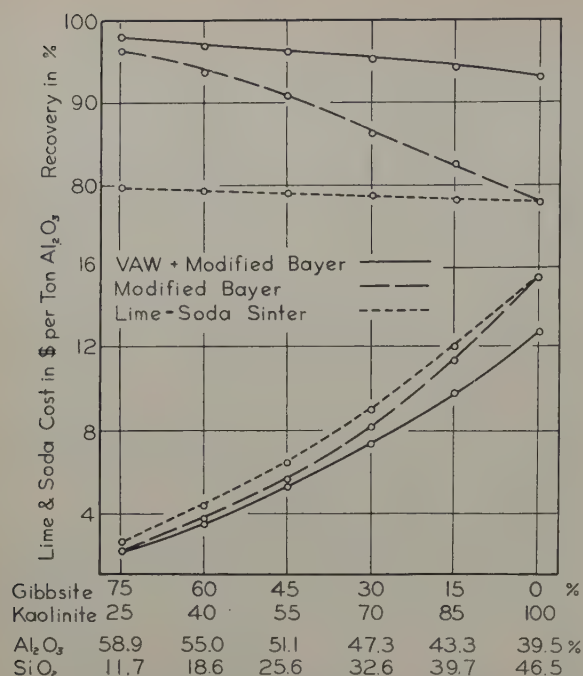


Fig. 1—Influence of silica content of ore on alumina recovery and reagent costs.

6 pct silica. The need for further investigation with variable leaching conditions is indicated by the removal of 10 pct alumina during desilication.

When calcination of the halloysite at 950°C (1742°F) was lengthened from 2 to 4 hr, silica extraction was improved without materially affecting the solubility of the alumina, and the alumina soluble by pressure digestion was increased. Raising the temperature of calcination of the kaolinite from 950° to 1000°C (1742° to 1832°F) decreased the alumina removal without affecting the silica extraction and somewhat increased the available alumina.

There are differences of opinion concerning the material resulting from the dehydration of hydrous aluminum silicates. Insley and Ewell<sup>16</sup> state that amorphous silica and amorphous alumina are formed; Vernadskii<sup>17</sup> says that kaolin anhydride is produced; and Hyslop<sup>18</sup> considers that kaolinite completely breaks down around 600°C (1112°F) to form a silicate stable to about 900°C (1652°F). X-ray examination of calcines and desilicated residues in this investigation shows that an amorphous condition follows dehydration. Calcines prepared at 600° to 800°C (1112° to 1472°F) were as resistant to increased silica extraction with 10 pct caustic as those produced at 400° and 500°C (752° and 932°F).

Experiments were conducted on the dehydration of halloysite under reduced pressures and lower temperatures in order to investigate the properties of the resulting products. It was thought that the release of chemically combined water under such conditions might yield a product more amenable to desilication. However, these calcines gave no definite X-ray patterns, and there was no material difference in their solubility from those produced under normal conditions.

X-ray patterns of calcines and leach residues showed the presence of mullite when calcinations above 900°C (1652°F) were made. Though quantitative measurements were not made, the amount of mullite appeared to increase with higher temperatures and longer calcination. The formation of mullite in the desilication process has not been reported

previously, although its presence in fired kaolinite has been reported by other investigators.<sup>19-21</sup> Comofore, Fischer, and Bradley<sup>22</sup> describe the formation of mullite as due to the collapse of a noncrystalline skeletal anhydride to produce a more stable crystalline form when kaolinite is fired to approximately 1000°C (1832°F). The formation of mullite renders a portion of the silica resistant to the caustic treatment and probably causes some reduction in available alumina. X-ray diffraction also reveals the presence of  $\gamma$  alumina in the calcines and leach residues.

The results of the preliminary work on kaolinite show that by calcination and leaching with 10 pct caustic solution, 85 pct desilication may be expected with alumina losses of approximately 10 pct. Although the silica extraction is higher, the alumina losses are substantially greater than those reported for the Vereinigte Aluminium-Werke process. The desilicated product, which averages 68 pct alumina, with slightly less than half of it soluble by pressure digestion, cannot be considered a suitable feed for the Bayer process. Consideration may be given to this material as a feed to either the combination or lime-soda process. The desilication treatment is also open to speculation if applied to ores of lower silica content. The preliminary results are considered definite enough to warrant additional fundamental investigations with variable conditions of calcination to minimize the formation of mullite, and also with leaching procedures to reduce alumina losses in desilication.

In addition to kaolinite, bauxitic and kaolinitic clays with various amounts of gibbsite (both in naturally occurring ores and synthetic mixtures) will be included in future investigations. The calcination experiments will involve a more detailed consideration of heating rate as well as the temperature within the region of the exothermic reaction as determined by differential thermal analysis. Comparative tests will also be made on pelletized calcines, percolation, counterflow, and multiple-stage leaching, and determination of solution stabilities. These data will be necessary for a complete evaluation of the Vereinigte Aluminium-Werke process when applied to domestic high silica potential aluminum resources.

### Process Comparison

A comparison of the potential position of the Vereinigte Aluminium-Werke desilication process relative to the modified Bayer, or Alcoa combination process, and the lime-soda sinter processes was evaluated in terms of the especially significant factors, alumina recovery and reagent cost. Although the less tangible factors of labor, plant installation, and fuel costs would appreciably influence any economic analysis, these considerations were not included in the comparison. The German and Alcoa procedures utilize stages of the Bayer and lime-soda sinter processes, and assumptions for these common stages were the same. Hypothetical feeds containing proportions of kaolinite and gibbsite were used to simplify the comparison.

The chemical and physical principles of the Vereinigte Aluminium-Werke process are not thoroughly established; therefore, the best results from the published German tests<sup>11</sup> were used in the evaluation. In this work, 80 pct of the silica was extracted with an alumina loss of only 2 pct, and a lime consumption of 3 mols per mol of silica ex-



tracted was assumed in the comparison. The Bayer digestion was assumed to recover 100 pct of the alumina that was not converted to insoluble sodium aluminum silicate. Corresponding portions of alumina and soda were considered to be rejected to red mud. Although alumina recoveries for the lime-soda sinter process of 86 to 89 pct have been obtained,<sup>6</sup> other authorities have expressed the opinion that commercial operations using high silica feeds would approach an alumina recovery of 80 pct. Although the latter figure may be slightly pessimistic, it was assumed for the calculations along with a rejection of 98 pct of the silica to the brown mud, a lime consumption of 200 pct, and a soda consumption equivalent to 7 pct of the silica removed.

The calculations are based on the treatment of the residue from the German desilication procedure by an appropriate Bayer digestion, the red mud from which would be re-treated by a lime-soda sinter and the leach liquor returned to the Bayer digestion. Calculations for the modified Bayer are on the normal flow circuit. Those for the lime-soda sinter are based upon the alumina being extracted by Bayer digestion. To provide a basis for comparison, lime requirements were converted to limestone at an assumed value of \$2 a ton, and soda ash was valued at \$24 a ton (f.o.b. August 1950). Trends resulting from these estimates are illustrated in Fig. 1, which plots alumina recovery and reagent costs against increasing silica content of the ore.

Estimated alumina recovery from the modified Bayer process decreases rapidly, and reagent cost increases over sixfold as the silica content of the ore increases. If ore is fed directly to a lime-soda sinter plant, alumina recovery is relatively unaffected by increased silica content in the ore, and recovery cannot be expected to exceed 80 pct due to a 20 pct alumina loss in the first step of the process. Reagent costs for the direct lime-soda process are slightly higher than for the modified Bayer. Although alumina recovery for all processes decreases as the silica content of the ore increases, the recovery curve of the VAW process is the least affected. As a result of higher alumina recovery, the reagent costs of the VAW process are the most favorable.

Consideration may be given to the curves on the basis of an assumed alumina recovery in the lime-soda process of 90 pct. The recovery curve of the lime-soda sinter method would be displaced about 10 pct upward. As the modified Bayer and Vereinigte Aluminium-Werke calculations also depend on alumina recovery of the lime-soda sinter procedure, a proportional upward shift in these curves would also be obtained. Similarly, the reagent cost curves would be displaced downward for each process. It is then apparent that the absolute location of each curve depends on rather arbitrary assumptions, but the relative slope and relative position of each curve is inherently characteristic of the process.

### Conclusions

Mineral-dressing methods are limited in their present technology by the colloidal character of the ore and the chemical association of alumina with silica in clays. When necessity requires the use of varied and complex ores, classification techniques that depend on physical differences of the materials may be useful for rejecting impurities to produce a smaller volume of feed of superior quality for subsequent extractive operations.

Any alkaline process will require large tonnages

of high calcium limestone in the vicinity of the treatment plant to treat high silica ore. Direct feed of ore to a lime-sinter process is believed, by one school of thought, to be the best method currently available for treating high silica ore, as it avoids the large circulating load of soda.

Although there may be no technical limit to the modified Bayer process, as some authorities maintain, current economics dictate 13 pct as the maximum silica content in the ore unless soda is regenerated by carbonation, in which case 18 pct silica is the maximum. The increased tonnage of red mud caused by high silica ore reduces the tonnage of alumina that can be produced from an installation of a given sinter-plant capacity. If the VAW desilication procedure is capable of yielding a suitable feed to a Bayer process, the silica limit of aluminum ore could again be increased significantly with a subsequent expansion of available domestic resources.

An industrial and military preparedness program requires consideration of suddenly disrupted imports and ultimate depletion of domestic high grade bauxite. The technology of winning aluminum from domestic clays must be developed to meet such circumstances.

Further consideration of the Vereinigte process should include a more detailed study of conditions for calcination of kaolinitic and bauxitic clays to minimize mullitization, and an investigation of various leaching procedures to lessen alumina losses during desilication. Pilot-plant operations should follow promising laboratory experimental results and economic evaluations before commercial applications are considered.

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Technical Note

Crystallographic Angles for Tin

by J. F. Nicholas

THE angles between the crystallographic planes in cubic metals were originally given by Bozorth<sup>1</sup> and have been republished many times. Recently, Salkovitz<sup>2</sup> tabulated the angles for the hexagonal metals (magnesium, zinc, and cadmium). The most commonly used metal which does not fall into either of these groups is tin, which has a tetragonal structure with an axial ratio of  $c/a = 0.54558$  (99.99 pct purity, 25°C).<sup>3</sup> Accordingly, Table I has been prepared giving the possible values for the angle,  $\phi$ , between planes of the types  $\{HKL\}$  and  $\{hkl\}$ . The formula used was:

$$\cos \phi = \frac{Hh + Kk + Ll \frac{a^2}{c^2}}{\left[ \left( H^2 + K^2 + L^2 \frac{a^2}{c^2} \right) \left( h^2 + k^2 + l^2 \frac{a^2}{c^2} \right) \right]^{1/2}}$$

All angles are given correct to the nearest minute as this is sufficient for all practical purposes. Every angle depends in a different way on variations in the value of  $c/a$ , but even in the worst cases a variation of about 0.0003 in this ratio is needed to vary an angle by 1', which corresponds to a temperature change of 20°C or can be caused by impurities.

References

<sup>1</sup> R. M. Bozorth: *Physical Review* (1925) **26**, p. 390.

<sup>2</sup> E. I. Salkovitz: *JOURNAL OF METALS* (January 1951), *Trans. AIME*, p. 64; Correction (October 1951), p. 880.

<sup>3</sup> E. R. Jette and F. Foote: *Journal of Chemical Physics* (1935) **3**, p. 605.

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Table I. Angles between the Crystallographic Planes in Tetragonal Tin

| {HKL} |     | {hkl} |         | Angles between<br>Planes of Types<br>{HKL} and {hkl} | {HKL} |     | {hkl}   |         | Angles between<br>Planes of Types<br>{HKL} and {hkl} |
|-------|-----|-------|---------|------------------------------------------------------|-------|-----|---------|---------|------------------------------------------------------|
| 001   | 100 | 100   | 90°     |                                                      | 111   | 111 | 0°      | 51° 11' | 75° 18'                                              |
|       | 101 | 101   | 28° 37' |                                                      |       | 112 | 16° 33' | 42° 23' | 58° 45'                                              |
|       | 110 | 110   | 90°     |                                                      |       | 211 | 18° 11' | 49° 22' | 69° 22'                                              |
|       | 111 | 111   | 37° 39' |                                                      |       |     | 86° 55' |         |                                                      |
|       | 112 | 112   | 21° 6'  |                                                      |       | 301 | 38° 37' | 87° 28' |                                                      |
|       | 211 | 211   | 50° 40' |                                                      |       | 113 | 23° 14' | 39° 56' | 52° 5'                                               |
|       | 301 | 301   | 58° 35' |                                                      |       | 311 | 29° 34' | 50° 42' | 80° 45'                                              |
|       | 113 | 113   | 14° 25' |                                                      |       |     | 85° 40' |         |                                                      |
| 100   | 100 | 100   | 0°      | 90°                                                  | 112   | 112 | 0°      | 29° 29' | 42° 11'                                              |
|       | 101 | 101   | 61° 23' | 90°                                                  |       | 211 | 31° 11' | 47° 12' | 59° 46'                                              |
|       | 110 | 110   | 45°     |                                                      |       |     | 70° 53' |         |                                                      |
|       | 111 | 111   | 64° 24' |                                                      |       | 301 | 45° 17' | 74° 23' |                                                      |
|       | 112 | 112   | 75° 15' |                                                      |       | 113 | 6° 40'  | 25° 22' | 35° 31'                                              |
|       | 211 | 211   | 46° 14' | 69° 46'                                              |       | 311 | 41° 43' | 52° 37' | 70° 48'                                              |
|       | 301 | 301   | 31° 25' | 90°                                                  |       |     | 79° 5'  |         |                                                      |
|       | 113 | 113   | 79° 51' |                                                      | 211   | 211 | 0°      | 28° 19' | 40° 28'                                              |
| 101   | 101 | 101   | 0°      | 39° 35'                                              |       |     | 66° 18' | 78° 41' | 85° 36'                                              |
|       | 110 | 110   | 70° 12' |                                                      |       |     | 87° 32' |         |                                                      |
|       | 111 | 111   | 25° 36' | 60° 47'                                              |       | 301 | 22° 57' | 51° 16' | 74° 57'                                              |
|       | 112 | 112   | 19° 48' | 45° 48'                                              |       | 113 | 37° 11' | 47° 33' | 56° 25'                                              |
|       | 211 | 211   | 27° 24' | 43° 46'                                              |       | 311 | 64° 27' | 37° 43' | 65° 38'                                              |
|       |     |       | 67° 0'  | 76° 59'                                              |       |     | 69° 51' | 77° 6'  | 81° 4'                                               |
|       | 301 | 301   | 29° 58' | 62° 46'                                              | 301   | 301 | 0°      | 62° 51' | 74° 14'                                              |
|       | 113 | 113   | 20° 51' | 40° 1'                                               |       | 113 | 49° 4'  | 69° 14' |                                                      |
| 110   | 100 | 100   | 33° 34' | 55° 10'                                              |       | 311 | 15° 53' | 60° 20' | 63° 58'                                              |
|       | 101 | 101   | 71° 59' | 87° 18'                                              |       |     | 88° 24' |         |                                                      |
|       | 110 | 110   | 0°      | 90°                                                  | 113   | 113 | 0°      | 20° 17' | 28° 51'                                              |
|       | 111 | 111   | 52° 21' | 90°                                                  |       | 311 | 47° 17' | 54° 24' | 67° 5'                                               |
|       | 112 | 112   | 68° 54' | 90°                                                  |       |     | 72° 58' |         |                                                      |
|       | 211 | 211   | 42° 48' | 75° 51'                                              | 311   | 311 | 0°      | 31° 45' | 45° 32'                                              |
|       | 301 | 301   | 52° 53' |                                                      |       |     | 60° 12' | 69° 41' | 75° 26'                                              |
|       | 113 | 113   | 75° 35' | 90°                                                  |       |     | 78° 36' |         |                                                      |
|       | 311 | 311   | 39° 18' | 67° 14'                                              |       |     |         |         |                                                      |



# Mechanism of Grain Refinement in Aluminum Alloys

by F. A. Crossley and L. F. Mondolfo

The mechanism of grain refinement by the addition of small amounts of titanium, molybdenum, zirconium, tungsten, and chromium to aluminum was investigated. The results indicate that the grain refinement is caused by the peritectic reaction which, by transforming the intermetallic compound into crystals of aluminum solid solution, seeds the melt with nuclei above the freezing point of aluminum.

THE feasibility of reducing the grain size of aluminum alloy castings by the addition of small amounts of titanium, zirconium, molybdenum, tungsten, columbium, boron, and chromium has been known for a long time, and the use of some of these elements as grain refiners is common practice in the aluminum foundry industry. The purpose of the present investigation was to determine the mechanism by which these additions produce the grain refinement.

Asato et al.,<sup>1-5</sup> on the basis of extensive work on copper, antimony, and silver alloys, presented a theory of grain refinement based on the occurrence of the peritectic reaction. Briefly, this theory states that during cooling of the melt crystals of the primary phase form, which react peritectically with the liquid upon further cooling. The peritectic reaction transforms at least partially the primary crystals into crystals of the secondary phase, which then act as nuclei for solidification of the remaining melt. As the peritectic reaction takes place the primary crys-

tals break in pieces, and each piece acts as a nucleus. Fine dendritic crystals which can easily break are the most effective for grain refinement.

Sicha and Boehm,<sup>6</sup> in investigating the refining effect of titanium on an Al-Cu alloy, concluded that  $TiAl_3$  crystals serve as nuclei to initiate crystallization, but did not offer further information on the mechanism of refinement. Bonsack in the discussion of their paper suggested that refinement was due to clouds of some solid in the melt, probably  $TiO_2$  which hindered grain growth.

Eborall,<sup>7</sup> after studying the effect of titanium, zirconium, vanadium, tungsten, columbium, chromium, and boron on some alloys, concluded that the peritectic reaction was not an essential feature of grain refinement. Her conclusion was based mainly upon the observation that under her experimental conditions (sand casting) the Al-Cr alloys, which undergo a peritectic reaction, did not show appreciable refinement.

Cibula<sup>8</sup> investigated the mechanism of grain refinement and reported that two types of grain refinement exist: 1—Grain refinement produced by restriction of grain growth by the concentration gradient mechanism proposed by Northcott.<sup>9</sup> 2—Grain refinement produced by the presence of particles in the melt, upon which the melt crystallizes easily. He further concluded that very marked grain refinement results from a combination of the two mechanisms. Since  $TiC$  was found present in aluminum alloys refined by the addition of titanium, it was identified as the nucleating agent. In the case

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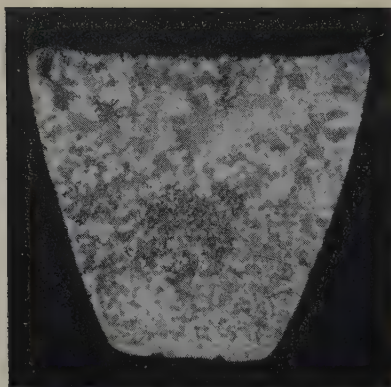


Fig. 1—Typical section of an ingot.  
Natural Size.

of the other refiners the identification of the nuclei as carbides was based on indirect evidence.

### Experimental Technique

The metals used in this investigation were high purity aluminum (99.90 pct) and other metals (at least 99 pct). In the experimental melts the alloying elements were so diluted that any impurity introduced by them was negligible.

The master alloys were prepared in zircon crucibles using an induction furnace, and the experimental melts were made in alumina crucibles at the start, but the less expensive clay crucibles, coated with sodium aluminate to prevent contamination, were later used for most of the investigation. Graphite crucibles were used for the alloys to which carbon was to be added. The experimental melts were made in electric resistance furnaces. For fluxing the alloys and wetting of the addition elements, Dow Chemical No. 230 was used. Argon gas of commercial purity, containing small amounts of oxygen and nitrogen, was introduced in some melts through alumina tubes.

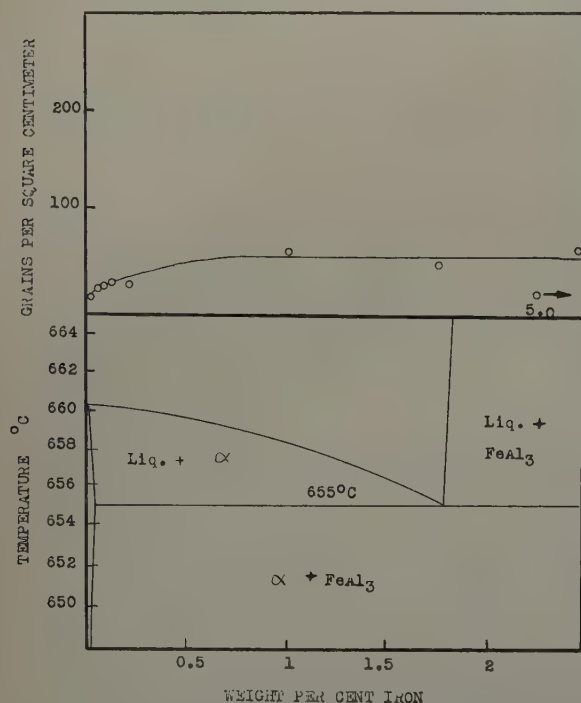


Fig. 2—Al-Fe equilibrium diagram and plot of grain size vs. composition of melt, series 3.

Table I. Composition and Analysis of Alloys

| Sam-<br>ple<br>No. | Aver-<br>age<br>Analy-<br>sis | Analysis<br>of Grain<br>Meas-<br>ure-<br>ment<br>Zone | Grain<br>Size<br>Grains<br>per<br>Sq Cm | Notes                                                                                                            |
|--------------------|-------------------------------|-------------------------------------------------------|-----------------------------------------|------------------------------------------------------------------------------------------------------------------|
| 00                 |                               |                                                       | 0.75                                    | Pure aluminum, furnace cooled from 100°C above the liquidus                                                      |
| 00a                |                               |                                                       | 0.70                                    | Pure aluminum, treated with argon 100°C above liquidus, furnace cooled                                           |
| 1-1                | 0.02 Zr                       |                                                       | 3                                       | Furnace cooled from 100°C above the liquidus, alumina crucibles                                                  |
| 1-2                | 0.06 Zr                       |                                                       | 2                                       |                                                                                                                  |
| 1-3                | 0.08 Zr                       |                                                       | 3.5                                     |                                                                                                                  |
| 1-4                | 0.12 Zr                       |                                                       | 9.5                                     |                                                                                                                  |
| 1-5                | 0.12 Zr                       |                                                       | 32                                      |                                                                                                                  |
| 1-10               | 0.14 Zr                       |                                                       | 58                                      |                                                                                                                  |
| 1-9                | 0.15 Zr                       |                                                       | 28                                      |                                                                                                                  |
| 1-6                | 0.40 Zr                       | 0.41                                                  | 314                                     |                                                                                                                  |
| 1-11               | 1.02 Zr                       |                                                       | 58                                      |                                                                                                                  |
| 2-1                | 0.05 Ti                       |                                                       | 36                                      | Furnace cooled from 100°C above the liquidus, graphite crucibles                                                 |
| 2-2                | 0.09 Ti                       |                                                       | 56                                      |                                                                                                                  |
| 2-3                | 0.14 Ti                       |                                                       | 94                                      |                                                                                                                  |
| 2-4                | 0.19 Ti                       |                                                       | 117                                     |                                                                                                                  |
| 2-5                | 0.23 Ti                       |                                                       | 238                                     |                                                                                                                  |
| 2-6                | 0.28 Ti                       |                                                       | 164                                     |                                                                                                                  |
| 2-7                | 0.47 Ti                       | 0.462                                                 | 168                                     |                                                                                                                  |
| 2-8                | 0.94 Ti                       | 1.12                                                  | 92                                      |                                                                                                                  |
| 3-9                | 0.01 Fe                       |                                                       | 13                                      | Furnace cooled from 100°C above the liquidus, coated clay crucibles                                              |
| 3-8                | 0.04 Fe                       |                                                       | 21                                      |                                                                                                                  |
| 3-7                | 0.07 Fe                       |                                                       | 22                                      |                                                                                                                  |
| 3-6                | 0.10 Fe                       |                                                       | 23                                      |                                                                                                                  |
| 3-5                | 0.20 Fe                       |                                                       | 17                                      |                                                                                                                  |
| 3-4                | 1.00 Fe                       | 0.995                                                 | 53                                      |                                                                                                                  |
| 3-3                | 1.80 Fe                       |                                                       | 36                                      |                                                                                                                  |
| 3-2                | 2.50 Fe                       |                                                       | 63                                      |                                                                                                                  |
| 3-1                | 5.01 Fe                       | 5.07                                                  | 9                                       |                                                                                                                  |
| 4-1                | 0.20 Cr                       |                                                       | 30                                      | Furnace cooled from 100°C above the liquidus, coated clay crucibles                                              |
| 4-2                | 0.30 Cr                       |                                                       | 20                                      |                                                                                                                  |
| 4-3                | 0.40 Cr                       |                                                       | 34                                      |                                                                                                                  |
| 4-6                | 0.78 Cr                       | 0.81                                                  | 205                                     |                                                                                                                  |
| 4-7                | 1.55 Cr                       |                                                       | 88                                      |                                                                                                                  |
| 5-4                | 0.17 W                        |                                                       | 24                                      | Furnace cooled from 100°C above the liquidus, alumina crucibles                                                  |
| 5-3                | 0.30 W                        |                                                       | 35                                      |                                                                                                                  |
| 5-5                | 0.39 W                        |                                                       | 101                                     |                                                                                                                  |
| 5-2                | 0.55 W                        | 0.57                                                  | 234                                     |                                                                                                                  |
| 5-1                | 1.23 W                        |                                                       | 48                                      |                                                                                                                  |
| 6-4                | 0.08 Mo                       |                                                       | 16                                      | Furnace cooled from 100°C above the liquidus, coated clay crucibles                                              |
| 6-3                | 0.20 Mo                       |                                                       | 52                                      |                                                                                                                  |
| 6-2                | 0.41 Mo                       |                                                       | 167                                     |                                                                                                                  |
| 6-1                | 0.79 Mo                       | 0.84                                                  | 211                                     |                                                                                                                  |
| 7-1                | 0.03 Ti                       | 0.029                                                 | 6.2                                     | Furnace cooled from 100°C above the liquidus, melts 1 to 7 in alumina crucibles, others in coated clay crucibles |
| 7-17               | 0.07 Ti                       | 0.073                                                 | 26                                      |                                                                                                                  |
| 7-2                | 0.10 Ti                       | 0.098                                                 | 50                                      |                                                                                                                  |
| 7-3                | 0.13 Ti                       | 0.118                                                 | 66                                      |                                                                                                                  |
| 7-4                | 0.15 Ti                       | 0.146                                                 | 139                                     |                                                                                                                  |
| 7-15               | 0.18 Ti                       |                                                       | 211                                     |                                                                                                                  |
| 7-13               | 0.20 Ti                       |                                                       | 256                                     |                                                                                                                  |
| 7-16               | 0.22 Ti                       | 0.191                                                 | 248                                     |                                                                                                                  |
| 7-12               | 0.24 Ti                       | 0.238                                                 | 354                                     | Treated with argon at 100°C above the liquidus, then furnace cooled in coated clay crucibles.                    |
| 7-14               | 0.30 Ti                       | 0.280                                                 | 418                                     |                                                                                                                  |
| 7-10               | 0.32 Ti                       | 0.323                                                 | 576                                     |                                                                                                                  |
| 7-11               | 0.37 Ti                       | 0.384                                                 | 1080                                    |                                                                                                                  |
| 7-5                | 0.39 Ti                       | 0.385                                                 | 840                                     |                                                                                                                  |
| 7-9                | 1.10 Ti                       | 1.27                                                  | 754                                     |                                                                                                                  |
| 7-7                | 1.75 Ti                       | 2.29                                                  | 222                                     |                                                                                                                  |
| 7-1a               | 0.07 Ti                       | 0.068                                                 | 21                                      | Held ½ hr at 850°C, Al <sub>2</sub> C <sub>3</sub> stirred in melt, furnace cooled, graphite crucible            |
| 7-2a               | 0.13 Ti                       |                                                       | 26                                      |                                                                                                                  |
| 7-3a               | 0.22 Ti                       |                                                       | 85                                      |                                                                                                                  |
| 7-4a               | 0.29 Ti                       |                                                       | 158                                     |                                                                                                                  |
| 7-5a               | 0.40 Ti                       |                                                       | 303                                     |                                                                                                                  |
| 7-6a               | 0.75 Ti                       | 0.82                                                  | 445                                     |                                                                                                                  |
| 7-8a               | 1.53 Ti                       |                                                       | 56                                      |                                                                                                                  |
| 2-1c               | 0.32 Ti                       |                                                       | 60                                      | Same as above, except that graphite instead of carbide                                                           |
| 2-2c               | 0.32 Ti                       | 0.314                                                 | 71                                      |                                                                                                                  |
| 2-3c               | 0.52 Ti                       |                                                       | 56                                      |                                                                                                                  |

The experimental melts were prepared by adding the required amount of master alloy to molten aluminum. When the melt reached a temperature 100°C above the liquidus it was stirred for a few minutes and then allowed to cool in the furnace. The rate of cooling was determined to be 6° to 7°C per min.



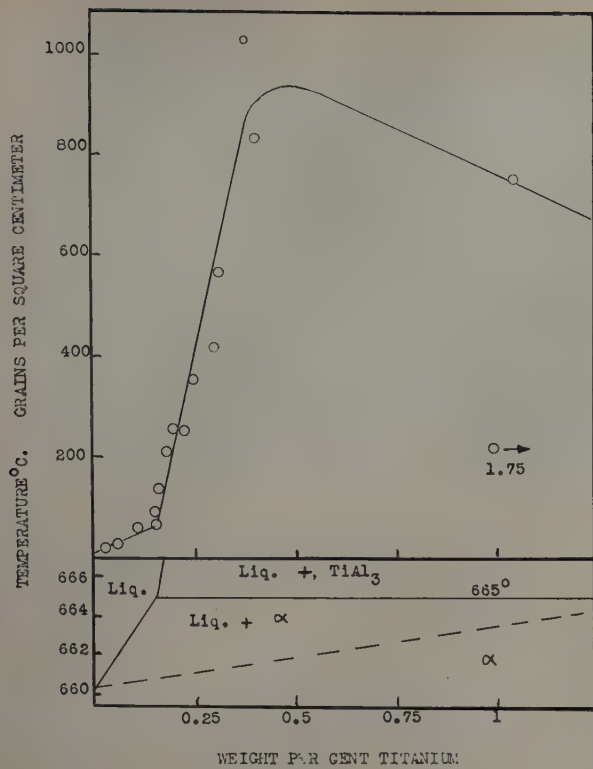


Fig. 3—Al-Ti equilibrium diagram and plot of grain size vs. composition of melt, series 7.

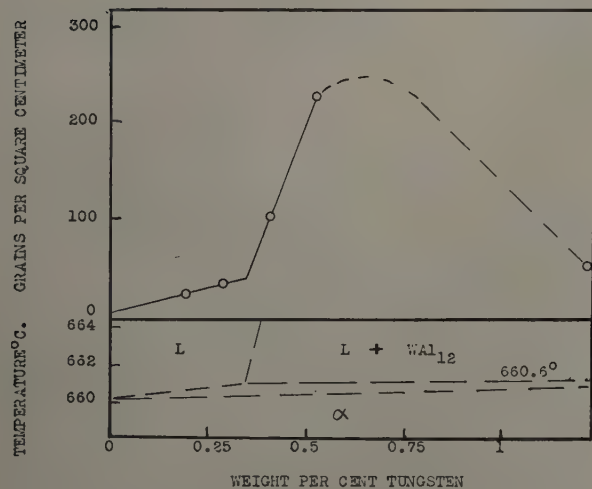


Fig. 4—Al-W equilibrium diagram and plot of grain size vs. composition of melt, series 5.

Five series of alloys were run this way, one for each of the alloying elements. Another series of Al-Ti alloys was treated with argon at the maximum temperature. The argon gas was bubbled through the melt for 30 sec, then the alloys were furnace cooled as usual. A third series of Al-Ti alloys was run in graphite crucibles, using the same technique as for the alloys discussed before. In addition three more melts were made in graphite crucibles using special techniques to increase the amount of carbon in the alloys. One melt containing 0.32 pct Ti was held at 850°C (approximately 100°C above the liquidus temperature) for 30 min. During this time aluminum carbide was stirred into it. This was followed by furnace cooling. The second melt, also containing 0.32 pct Ti, was treated in a similar way, but

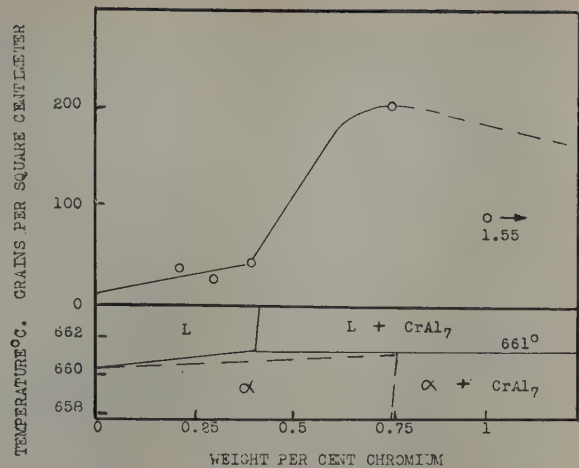


Fig. 5—Al-Cr equilibrium diagram and plot of grain size vs. composition of melt, series 4.

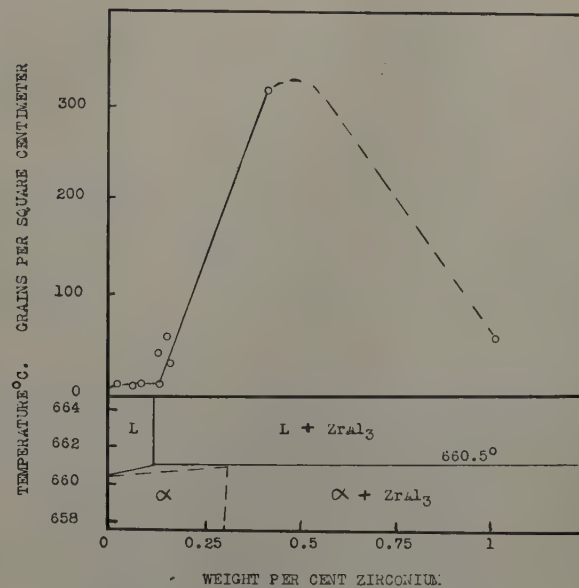


Fig. 6—Al-Zr equilibrium diagram and plot of grain size vs. composition of melt, series 1.

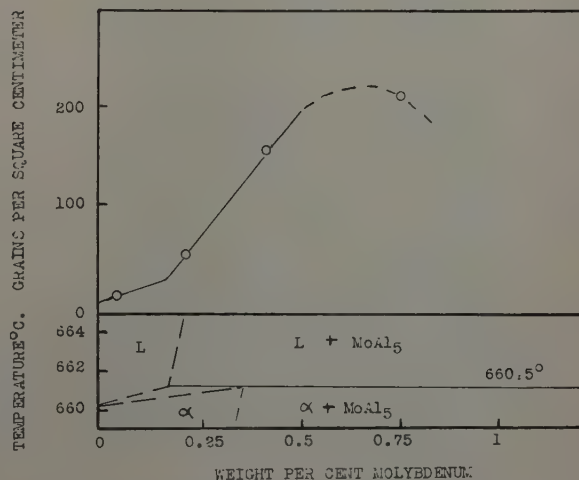


Fig. 7—Al-Mo equilibrium diagram and plot of grain size vs. composition of melt, series 6.



Fig. 8—Nucleation by  $\text{TiAl}_3$ . Etched with 1 pct HF-1.5 pct Ti, slow cooled in furnace. X25.

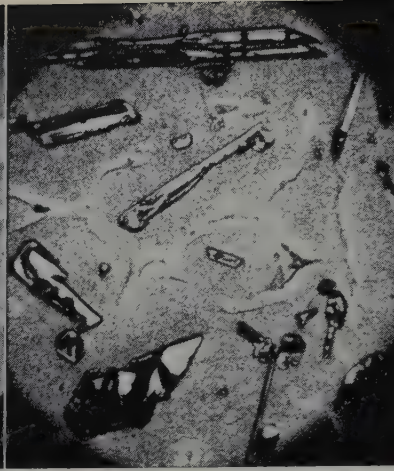


Fig. 9—Nucleation by  $\text{CrAl}_2$ . Etched with 1 pct HF-1.79 pct Cr, slow cooled in furnace. X50.

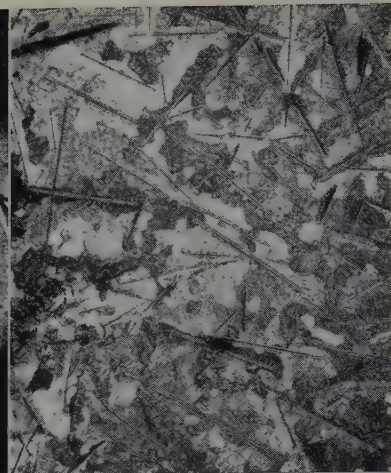


Fig. 10—Nucleation by  $\text{TiAl}_3$ . Etched with 1 pct HF-1.75 pct Ti, slow cooled in furnace. X5.

graphite, instead of carbide, was stirred into it. The third melt, containing 0.50 pct Ti, was held at  $900^\circ\text{C}$  for  $2\frac{1}{2}$  hr in a graphite crucible, stirred thoroughly, and then furnace cooled.

The solidified specimens from all these melts had the approximate size and shape shown in Fig. 1.

Some of the grindings that resulted when the specimens were cut and faced were analyzed by wet methods. In most alloys the difference between these analyses and the nominal ones was within the error of analysis (approximately 0.01 pct). The zirconium-bearing alloys, however, showed large losses of zirconium, and for this reason all of them were analyzed. The nominal compositions or, when available, the actual analyses are reported in col. 2, Table I.

After the melts had solidified and they were examined for grain size, other spot checks for composition were run. The grain size count was done in all specimens at the same distance from the bottom, along a horizontal line. Drillings were then taken along this line with a  $\frac{1}{8}$ -in. drill and analyzed. This was done because segregation of primary crystals was evident in some alloys. These analyses revealed that segregation was appreciable only in the alloys

with an alloying content above 1 pct. For the other alloys the difference between the nominal analysis and the analysis of the zone where the grain determination was done was within the error of analysis. These analyses are reported in col. 3 of Table I.

The ingots were sectioned vertically at the center, and the grain size of the specimens was measured by counting the grains intercepted by a line running horizontally on the polished face 0.3 in. from the bottom. Great care was taken to position this line exactly on the specimens, since variations of grain size were found from top to bottom of the melts, as shown in Fig. 1.

## Results and Discussion

In Figs. 2 to 7 are shown the effects of increasing additions of the elements on the grain size, as related to the equilibrium diagrams. Dashed lines have been used when the data are uncertain.

In the Al-Fe alloys, as the iron content was increased, the grain size decreased slightly with the first additions of iron, remained fairly constant over a wide range, well past the eutectic point, and then slowly increased. At the lower concentrations the other alloys behaved similarly, but when the composition was reached, at which the peritectic reaction occurred, a marked grain refinement appeared; and there was a sharp change in the slope of the grain size curve. With increasing additions beyond the start of the peritectic reaction, the grain refinement reached a maximum and then decreased.

At the point where the first change in slope of the grain size curve took place, primary crystals of intermetallic compound were formed. However, the presence of primary crystals per se could not be the cause of grain refinement, since in the hypereutectic Al-Fe alloys the same effect could not be noticed. Thus, the evidence points to the peritectic reaction as the cause of the grain refinement.

The above supposition found good confirmation from the microexamination. As shown in Figs. 8 to 10, the primary crystals of intermetallic compound were found inside the crystal, and the dendrites of aluminum solid solution appeared to center on them. Some of the dendrites did not show primary crystals. However, this can be explained by assuming that either the primary crystal was not in the plane of

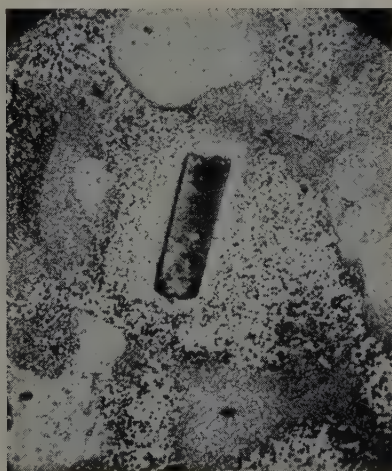


Fig. 11—Shape of primary crystals of  $\text{TiAl}_3$  when rapidly frozen 1.3 pct Ti poured in water. Etched with 1 pct HF. X700.



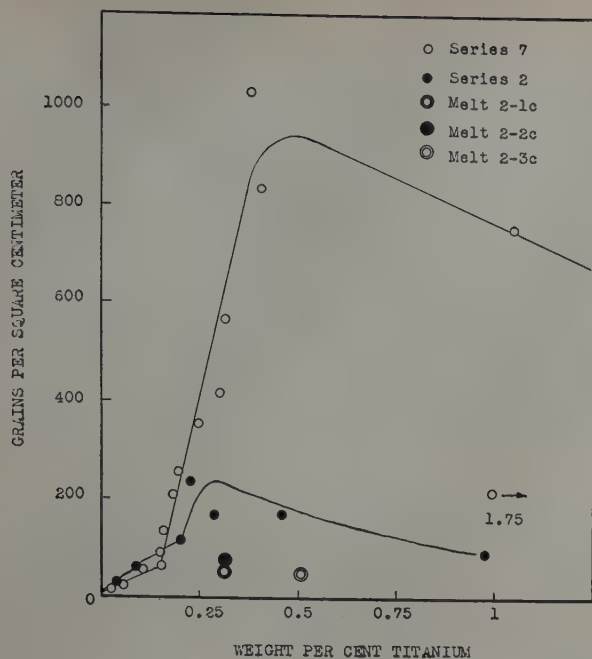


Fig. 12—Effect of carbon additions on the grain size of Al-Ti alloys.

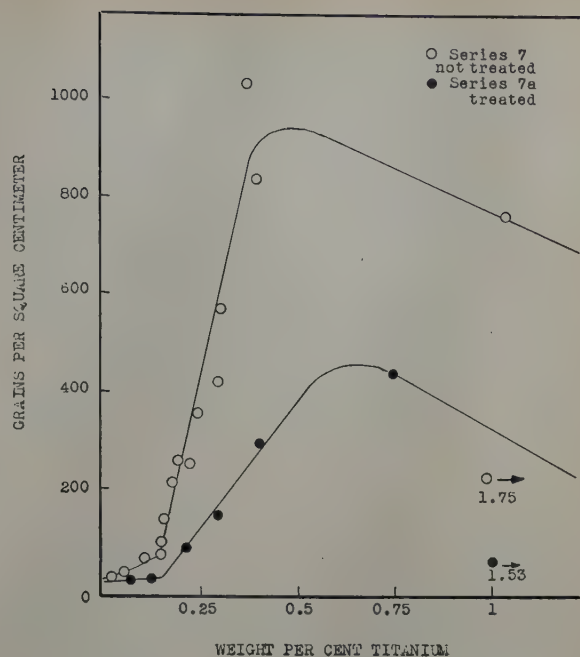


Fig. 13—Effect of treating with argon gas on the grain size of Al-Ti alloys.

the section, or the peritectic reaction was completed and the primary crystal was consumed. Fig. 10 shows the same type of distribution of primary crystals and in addition shows that, when the number of primary crystals was sufficient, practically every grain surrounded a primary crystal. The micrographs shown are all of alloys with amounts of alloying element well above the beginning of the peritectic reaction. This was necessarily so, because with lower contents the primary crystals were completely consumed and disappeared. This explains the relatively coarse grain size in the micrographs.

The same type of evidence for nucleation was also found in the other systems (with the exception of the Al-Fe), although in some cases the evidence was not as clear as in the examples shown. In the Al-Zr and Al-W alloys it was not possible to develop the dendritic structure well enough to photograph it, although evidence of nucleation around the primary crystals was visible when the alloys were strongly over-etched.

Extensive microexamination was conducted to determine if fragmentation of the primary crystals played a significant role in the refinement. It was found that the intermetallic compounds formed by the grain refiners investigated tended to have a platelike (needles in section) structure, rather than the dendritic structure deemed necessary for fragmentation by Asato et al. Even very rapid cooling did not appreciably change the form of the primary crystals, as evidenced by Fig. 11. Cracking of the primary crystals was sometimes observed (Fig. 8) and there was some evidence that occasionally the pieces of a primary crystal, when broken, nucleated two or more grains. However, this phenomenon was found in very few cases and did not seem to play an important part in the grain refinement.

In Fig. 12 are plotted the results of experiments run in the presence of carbon. Three sets of results are plotted: 1—melts in which the introduction of carbon was carefully avoided (series 7); 2—melts in which some carbon was absorbed from the graphite crucibles (series 2); and 3—melts in which an effort

was made to introduce large amounts of carbon (melts 2-1c, 2-2c, 2-3c). The grain size of the alloys in which no peritectic reaction occurred was not appreciably affected by the addition of carbon. In the alloys undergoing the peritectic reaction the effect of carbon additions was very pronounced and the grain refining effect was greatly reduced, and even disappeared when sufficient carbon was present. These results are in direct opposition to Cibula's statement that TiC is the agent responsible for grain refinement, because if this were true, grain refinement should have increased with increasing carbon content. Instead, the suggestion is further substantiated that the peritectic reaction of  $\text{TiAl}_3$  with the liquid was responsible for the grain refinement. The addition of carbon, by tying up the titanium as TiC, prevented the formation of  $\text{TiAl}_3$ .

Hollomon and coworkers<sup>11</sup> and others<sup>12-16</sup> have demonstrated that solid impurities in a melt can act as



Fig. 14—Effect of number of primary crystals on grain size. At the bottom large amount of fine primary crystals, above few coarse primary crystals. Etched with 1 pct HF-1.5 pct Ti, slow cooled in furnace. X5.

centers for crystallization. Any treatment that reduces the amount of the solid impurities must result in a coarsening of the grain. This is clearly shown in Fig. 13. The alloys in which argon treatment had removed impurities solid above the liquidus temperature showed a much coarser grain than the non-treated alloys. However, the shape of the grain size curve was the same, thus indicating that, although the number of  $\text{TiAl}_3$  particles was reduced, their effect as nucleating agents was not lost. The dependence of the grain size on the number of primary crystals is also shown in Fig. 14. Because of gravity segregation a large number of primary crystals were concentrated in the bottom layer and the grain size there was very small, the layer above it contained only a few large primary crystals, and the grain size was coarse.

### Conclusions

Grain refinement in aluminum alloys by the addition of titanium, zirconium, molybdenum, chromium, and tungsten is associated with the peritectic reaction. The primary crystals of intermetallic compound which form, react with the liquid and become sheathed with a solid having the crystal structure of the phase that is going to be formed from the liquid. These solid particles act as nuclei for the crystallization of the melt, thus eliminating the necessity for undercooling to provide spontaneous nucleation.

In the case of the above elements, fragmentation of the primary crystals during peritectic reaction was not observed to an appreciable extent and consequently does not seem to play an important part in the grain refinement.

The final grain size appears to be mainly dependent on the number of primary crystals that form, and any factor which affects the number of these crystals will alter the grain size.

The addition of carbon to Al-Ti alloys reduces the grain refining effect, and the effect of the grain refining agent is lost if sufficient carbon is added.

Some grain refinement can be obtained by additions of the above elements in amounts insufficient to produce the peritectic reaction, or by the addition of other elements, but the effect is not as pronounced as when the peritectic reaction occurs.

### Summary

The mechanism of grain refinement by the addition of chromium, titanium, tungsten, molybdenum, zirconium, and iron was investigated. The first five elements, when present in sufficient amounts, formed

primary crystals which reacted peritectically with the liquid. The resulting solid particles acted to nucleate the solidification of the remaining liquid. This extra source of nucleation produced decided grain refinement in many cases. It was found that lesser amounts of the five elements and even large additions of iron only slightly reduced the grain size. No evidence of nucleation by primary crystals of  $\text{FeAl}_3$  was found. Upon these findings it was concluded that the peritectic reaction was necessary for decided grain refinement. No evidence was found that fragmentation of the primary crystals was of importance in producing the grain refinement, as reported by Asato et al. Removal of solid impurities and additions of carbon to the melt were found to decrease decidedly the grain refining effect.

### Acknowledgment

The authors gratefully acknowledge their indebtedness to the Apex Smelting Co. and to the Reynolds Metals Co. for the chemical analyses, to the Aluminum Co. of America for the high purity aluminum, to the Titanium Manufacturing Co. for the titanium and zirconium of high purity and the zircon crucibles. The authors also wish to thank the members of the staff and the students of the Department of Metallurgical Engineering of Illinois Institute of Technology, whose aid and suggestions were helpful in the course of this research.

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### Technical Note

## Surface Effect in the Cleavage of Zinc Monocrystals

by John J. Gilman

**S**URFACE effects in the brittle fracture of materials such as glass and in the plastic slip of zinc and cadmium crystals are well known.<sup>1</sup> Recently, another surface effect has been found for zinc monocrystals. It has been observed that certain normally ductile zinc monocrystals become ex-

tremely brittle when their surface is coated with a layer of oxide or copper plate.

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This phenomenon was first observed in a triangular zinc crystal which had been grown in a graphite mold surrounded by an atmosphere of air. The lowering rate during growth was 1 in. per hr and the temperature gradient in the furnace at the melting point was approximately 24°C per in. The raw zinc was chemically pure (99.999+ pct Zn). This crystal had a fairly thick (perhaps ½ mil thick) porous oxide coating as grown. Although its orientation was favorable ( $\chi$ , 46°;  $\lambda$ , 48°;  $\theta$ , 47°) for ductile bending, it cleaved without prior plastic deformation when loaded in bending. The load required for cleavage was appreciably greater when the maximum tensile stress was at the apex of the triangular cross-section nearest the slip direction than it was when the base of the triangle was in tension. The cleavages were good basal cleavages. However, the crystal was "optically mosaic," see Fig. 1 and Ref. 2; that is, the cleaved basal planes were not absolutely plane. They consisted of two or more very slightly disoriented regions as shown for a typical cleavage in Fig. 1.

In order to render this extremely brittle crystal very ductile it was only necessary to etch away the oxide layer. This was accomplished by a 10 min etch in 15 pct HCl. After this treatment the crystal could be bent completely around a 2 mm diam rod without cleavage.

A very similar effect was observed for two copper-plated crystals. These crystals were also triangular and of the same size (base of triangle is 0.210 in.), but they were grown in molds sealed inside evacuated pyrex tubes. They had the following orientation angles: crystal A— $\chi$ , 50°;  $\lambda$ , 50°;  $\theta$ , 49°; and crystal B— $\chi$ , 56°;  $\lambda$ , 56°;  $\theta$ , 63°.

Crystal A was cleaned with dilute HCl and then plated with a thin coating of copper for half of its length (7 in.). This copper coating was very fine grained and approximately 2200Å thick. When the crystal was loaded in tension the clean portion began to deform plastically at a resolved shear-stress of 32 g per sq mm, while the plated portion began to deform when the resolved shear stress reached 52 g per sq mm. Further loading caused additional plastic deformation until the plated portion of the crystal cleaved when the resolved normal stress was approximately 93 g per sq mm and the elongation in the plated portion was 2.5 pct. When the crystal was loaded in bending several days later the two portions of the crystal exhibited markedly different amounts of ductility. The amounts of bending which each portion could stand is shown in Fig. 2. The basal cleavages shown in Fig. 2 were optically mosaic just as those of the oxidized crystal.

Crystal B was cleaned with HCl and then plated with a film of copper approximately 5000Å thick. This crystal was very ductile when loaded in bending prior to the plating treatment. When it was loaded in bending a few hours after it had been plated it was very brittle. It had less ductility than crystal A after it had been plated. After the plate had been etched off with 25 pct HCl, the crystal was again ductile. In this case, also, when the basal cleavages were examined they were found to be optically mosaic.

These effects have not been found in all zinc crystals and, therefore, are tentatively associated

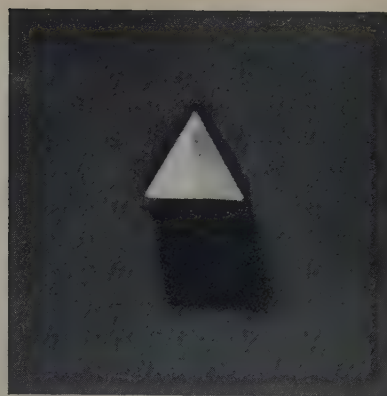


Fig. 1—Optically mosaic basal cleavage of a brittle triangular zinc crystal.



Fig. 2—Showing the difference in ductility between the copper-plated portion of crystal A and the clean portion. On the left is the plated half of the crystal.

with optically mosaic ones. However, the extreme change in ductility is produced by a change in the surface of the same crystal and to this extent is reproducible.

The phenomenological explanation of the effect might be as follows: The oxide or copper coating is very fine grained and therefore has little ductility. When the crystal is loaded in bending, brittle failure of the film creates a rift at the surface which starts cleavage along the basal plane of the zinc. Basal cleavage then propagates readily even though the crystal is ductile, just as it does if a razor blade is used as a wedge along a basal plane of a ductile zinc crystal. Another possible explanation is that the oxide coating or the copper plating inhibits slip so strongly that the critical normal stress for cleavage is reached before much slip can occur. The reason why some crystals do not behave in this way is not known. It may be that the surface effect is more subtle than those which are outlined above, but the present observations leave this as an open question.

#### Acknowledgment

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\* The angles are defined as follows:  $\gamma$  is the angle between slip plane and specimen axis;  $\lambda$ , the angle between slip direction and specimen axis; and  $\theta$ , the angle between slip direction and one surface normal.

# Constitution of Titanium-Aluminum Alloys

by H. R. Ogden, D. J. Maykuth, W. L. Finlay, and R. I. Jaffee

Aluminum has been found to be soluble in  $\alpha$  titanium to about 26 pct, and to raise the temperature range of transformation from  $\alpha$  to  $\beta$ . Two intermediate phases exist in the system, a new face-centered tetragonal phase, designated as  $\gamma$ , which occurs between 34 and 46 pct Al, and  $\text{TiAl}_3$ . Metallographic and X-ray diffraction data were used to determine the diagram.

**A**LUMINUM is one of the useful alloying additions for titanium-base alloys. It is an important constituent in two commercial alloys released in 1950, one containing 4 pct Al and 4 pct Mn, and the other containing 3 pct Al and 5 pct Cr as the metallic alloy content. It is probable that, in the future, other titanium alloys containing aluminum will be released. In the course of alloy development work, some of the features of the constitution of titanium-rich Ti-Al alloys have been developed. These are described in the present paper.

The only available information on the Ti-Al system concerns the aluminum-rich end of the diagram. In summarizing the early work, Hansen<sup>1</sup> indicated that there is little solubility of titanium in aluminum, and that a two-phase region exists up to the intermediate compound,  $\text{TiAl}_3$  (37.2 wt pct Ti), which has a congruent melting point at 1355°C. Fink<sup>2</sup> has reported that a peritectic reaction occurs at 665°C between the melt and  $\text{TiAl}_3$  to form the terminal solid solution of titanium in aluminum. The solubility of titanium in aluminum has been established at 0.24 pct at 510°C and is estimated to be between 1 and 1.5 pct at the peritectic temperature.

No information has been published on the diagram

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Table I. Analysis of Raw Materials Used

| Element | Analysis, Pct   |          |
|---------|-----------------|----------|
|         | Iodide Titanium | Aluminum |
| Fe      | <0.04           | 0.002    |
| Si      | <0.03           | 0.002    |
| Cu      |                 | 0.002    |
| Mg      |                 | 0.001    |
| N       | 0.005           |          |
| O       | 0.01            |          |
| C       | 0.03            |          |
| Al      | <0.05           | 99.99+   |
| Ti      | 99.85           |          |

above  $\text{TiAl}_3$ , other than a statement<sup>3</sup> that aluminum raises the  $\alpha$  to  $\beta$  transformation temperature of titanium.

## Materials and Preparation of Alloys

Iodide-type titanium and high-purity aluminum were used in this investigation. Typical analyses of these materials are given in Table I. Alloys were prepared by arc melting on a water-cooled copper hearth, using the techniques described previously for contamination-free melting.<sup>4</sup> Weight losses during melting were very low, ranging from 0 to 0.02 g in a 10 to 15 g charge, indicating that little or no loss of aluminum occurred during melting. This permitted the use of nominal compositions for these alloys.

Alloy ingots containing from 0 to 7.5 pct Al were rolled in air at 850°C to 0.040 in. sheet. Alloys containing from 7.5 to 16 pct Al could only be rolled about 25 pct reduction at temperatures up to and including 1200°C. Alloys containing above 16 pct Al



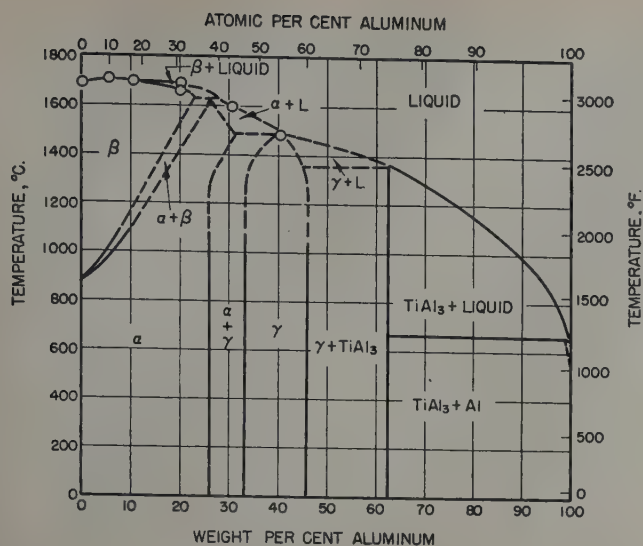


Fig. 1—Tentative diagram of the Ti-Al system.

were evaluated using cast ingots. The fabricated alloys were annealed for 3½ hr at 850°C in a vacuum of  $1 \times 10^{-4}$  mm Hg pressure before testing. After casting, the high aluminum alloys were given an homogenization anneal of 24 to 48 hr at 1000° to 1100°C before evaluation.

### Methods of Investigation

Alloy constitution was determined mainly by metallographic methods, supplemented by X-ray diffraction. For a few alloys, transition temperatures were checked using the inverse-rate method of thermal analysis. Melting temperatures of the titanium-rich alloys were obtained by observing the melting of an ingot with a hole drilled in it.

Heat treatments were done in a resistance furnace using an atmosphere of gettered argon. Temperature control was maintained at  $\pm 3^\circ\text{C}$  during the heat treatment. Iodide-titanium control samples showed no hardness increase after several hours at 1050°C, which indicated no contamination during heat treatment. The specimens were quenched into water from the heat-treatment temperature.

The metallographic specimens were mounted in bakelite, ground through 600X paper, and given a final polish with either diamond paste or jeweler's rouge on a wool lap. Etching was done with an aqueous solution of 3 pct  $\text{HNO}_3$ , 1½ pct  $\text{HF}$ .

All X-ray diffraction work was done on powder

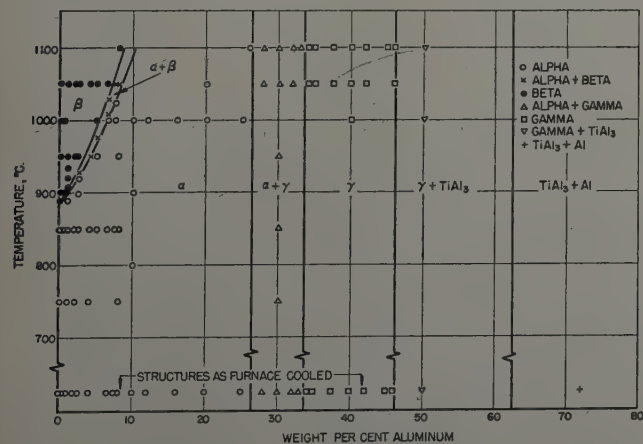


Fig. 2—Section of Ti-Al diagram showing data points.

samples. To avoid contamination during heat treatment, the alloy filings were kept in a hole drilled into a short length of as-deposited iodide-titanium rod, and capped with a titanium plug. This, in turn, was encapsulated in vacuum in Vycor. After heat treatment for the desired time and temperature, the Vycor capsule was quenched and broken under water.

The X-ray diffraction patterns on the powders were obtained using cobalt K radiation in a 57 mm Debye camera of the Buerger type with a Straumaius setting. An aluminum filter was inserted between the sample and the film to absorb scattered radiation. The lattice constants were calculated by the method of simultaneous equations from the quadratic form of the Bragg equation using the angular position of the (12.1) and the (11.4)  $\text{K}\alpha$  doublets, and, in alloys containing up to 7.5 pct Al, the (12.3)  $\text{K}\beta$  reflection.

In the melting point work, ingot samples were used which had a ⅛ in. hole drilled in them. These were supported by a molybdenum lining in a beryllia crucible and heated by induction in a vacuum furnace, using a graphite sleeve inductor. The temperature of the hole was observed continually with

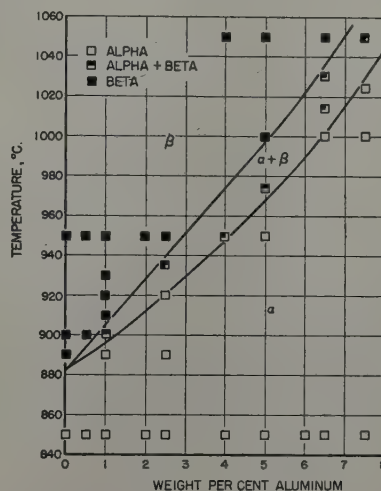


Fig. 3—Effect of aluminum on the transformation temperature of titanium.

an optical pyrometer, and the temperature at which the hole filled with molten metal was taken as the liquidus temperature. Solidus temperatures could be approximated by observing the temperature at which the edges of the hole started to round off.

### Constitution Diagram

A tentative diagram of the Ti-Al system is given in Fig. 1. The solid lines indicate the phase boundaries that have been established by this investigation between 0 and 50 pct Al and by others<sup>1, 2</sup> between 50 and 100 pct Al. Dashed lines indicate the probable equilibria in the areas not covered in this investigation, based on extrapolation of known data and pertinent observations discussed later in this paper. The solid equilibria section of the diagram covered by the present work is shown in Fig. 2, where data points indicate the results of microscopic examination. Fig. 3 shows the effect of aluminum on the transformation temperature of titanium between 0 and 7.5 pct Al in more detail. Aluminum is seen to cause a marked increase in the temperature range of the  $\alpha$ - $\beta$  transformation.

Thermal analysis produced an arrest at 888°C for



Fig. 4—Ti-5 pct Al alloy. X100.  
Annealed 3½ hr at 850°C and furnace cooled. Equiaxed  $\alpha$  grains.



Fig. 5—Ti-5 pct Al alloy. X100.  
Quenched after 30 min at 1000°C. Transformed  $\beta$  structure.



Fig. 6—Ti-5 pct Al alloy. X100.  
Quenched after 30 min at 975°C. Transformed  $\beta$  plus equiaxed  $\alpha$  structure.

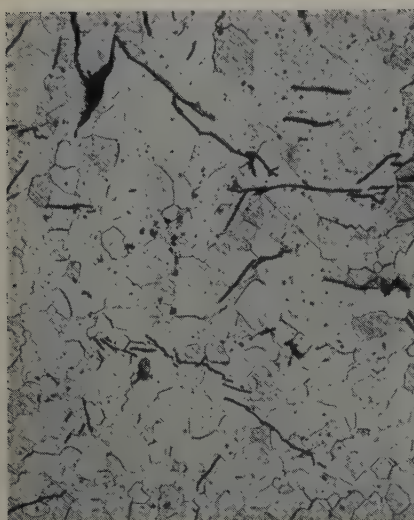


Fig. 7—Ti-16 pct Al alloy. X75.  
Rolled 25 pct at 1050°C and annealed 24 hr at 1000°C. Equiaxed  $\alpha$  grains.

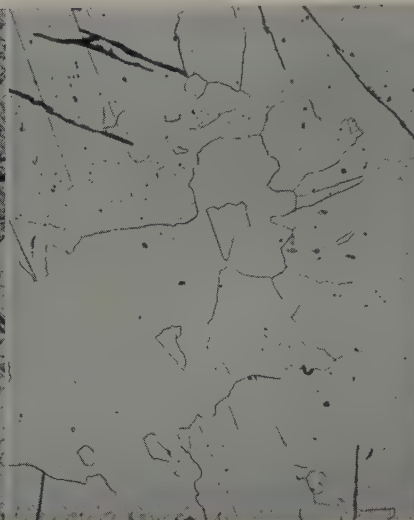


Fig. 8—Ti-20 pct Al alloy. X75.  
As-cast plus 24 hr at 1000°C. Serrated Widmanstätten plates of  $\alpha$ .

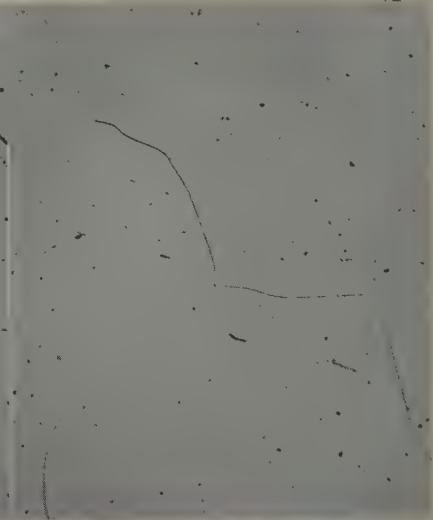


Fig. 9—Ti-25 pct Al alloy. X75.  
As-cast plus 24 hr at 1000°C. Equiaxed  $\alpha$  grains.

unalloyed titanium, at 964°C for a Ti-5 pct Al alloy, and at 1051°C for a Ti-8 pct Al alloy. These data confirmed the results of the metallographic work.

The melting point data obtained are given in Table II. The melting point obtained for pure titanium is considerably below the 1725°C melting point observed by De Boer.<sup>5</sup> This may have been the result of contamination from the carbon inductor. The melting point data obtained on the Ti-Al alloys fit better with 1725°C for the melting point of titanium. Also, they indicate a very slight decrease in melting point imparted by aluminum up to 20 pct Al. Above 20 pct Al, the melting point drops off much more rapidly.

Table II. Melting Point Data

| Wt, Pct Al | Incipient Melting, °C | Completely Molten, °C |
|------------|-----------------------|-----------------------|
| 0          | 1690                  | 1690                  |
| 5          | 1710                  | 1710                  |
| 10         | 1700                  | 1700                  |
| 20         | 1670                  | 1690                  |
| 30         |                       | 1600                  |
| 40         |                       | 1480                  |

The limit of solubility of aluminum in  $\alpha$  titanium has been established at about 26 pct between room temperature and 1100°C. The raising of the  $\alpha$ - $\beta$  transformation range by aluminum results in an extensive, but restricted,  $\beta$  field. With more than 26 pct Al, a new phase appears, and two-phase structures are found up to about 33 pct Al. Between 33 and 46 pct Al, a single-phase region occurs which has a face-centered tetragonal structure. This has been designated as the  $\gamma$  phase. The composition corresponding to TiAl<sub>3</sub>, 36 wt pct Al, is located within the  $\gamma$ -phase field. Above 46 pct Al, the TiAl<sub>3</sub> phase appears, which indicates that the two-phase region of  $\gamma$ -plus-TiAl<sub>3</sub> extends up to the composition limits of TiAl<sub>3</sub>.

The section of the diagram above 1050°C has been sketched in to show the probable equilibria at the higher temperatures. Since the melting point of titanium was found to be depressed only slightly by initial additions of aluminum, the extrapolation of the  $\alpha$  and  $\beta$  solvus lines would indicate a peritectic reaction occurring at a high temperature, at about 25 pct Al. The marked lowering of the melting point for the 30 and 40 pct Al alloys indicates that there





Fig. 10—Ti-28 pct Al alloy. X100.  
As-cast plus 24 hr at 1100°C. Banded  
structure of precipitated  $\gamma$  in  $\alpha$ .

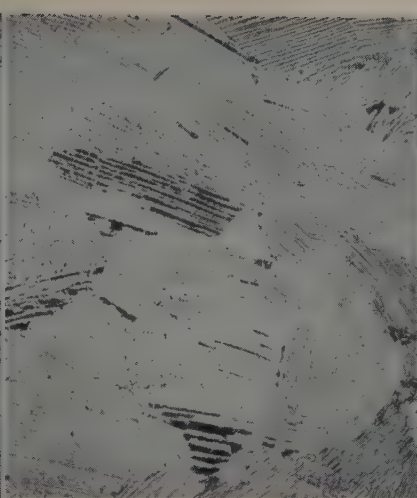


Fig. 11—Ti-30 pct Al alloy. X500.  
As-cast plus 24 hr at 1000°C. Banded  
structure of precipitated  $\gamma$  in  $\alpha$ .



Fig. 12—Ti-32 pct Al alloy. X100.  
As-cast plus 48 hr at 1100°C. Banded  
structure of  $\gamma$  precipitated in  $\alpha$  and  $\gamma$   
grains.

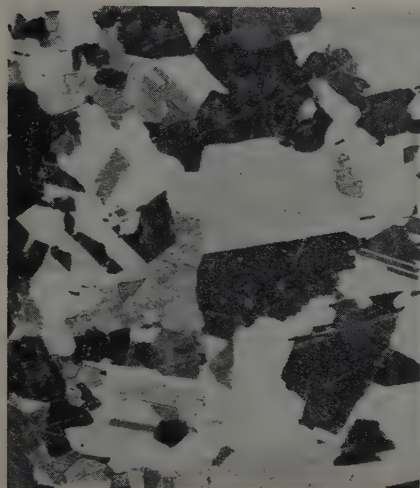


Fig. 13—Ti-34 pct Al alloy. X100.  
As-cast plus 48 hr at 1100°C.  $\gamma$  phase.



Fig. 14—Ti-46 pct Al alloy. X100.  
As-cast plus 48 hr at 1100°C. Cored  $\gamma$   
structure.

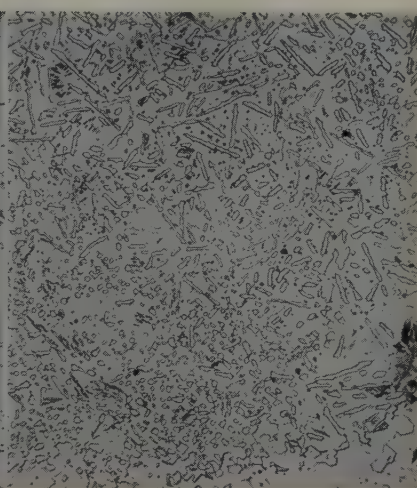


Fig. 15—Ti-50 pct Al alloy. X75.  
As-cast plus 48 hr at 1100°C.  $\gamma$  and TiAls.

is a second peritectic reaction between  $\alpha$  and liquid to form the  $\gamma$  phase. The melting point of the Ti-40 pct Al alloy has been established at about 1480°C, which is probably fairly close to the peritectic temperature. The increase in solubility of aluminum in  $\alpha$  titanium at the  $\gamma$  peritectic temperature has been based on the microstructure of the  $\alpha$ -plus- $\gamma$  alloys, wherein an  $\alpha$  decomposition product is obtained.

### Microstructures

The microstructures of Ti-Al alloys at low aluminum contents are similar to those of titanium. Alloys rolled and annealed at temperatures within the  $\alpha$  field have equiaxed  $\alpha$  grains similar to those found in high purity titanium given the same treatment. A typical structure of this type is shown in Fig. 4 for a Ti-5 pct Al alloy annealed at 850°C. Quenching the alloys from the  $\beta$  field results in a transformation structure of large, serrated Widmanstätten plates, very similar to that found with iodide titanium. This structure is shown in Fig. 5. The microstructure of alloys quenched from the  $\alpha$ -plus- $\beta$  field consists of a mixture of equiaxed  $\alpha$  grains and serrated Widmanstätten plates. This structure is dif-

ficult to interpret because of the similarity between the two types of grains. A typical structure is shown in Fig. 6 for a Ti-5 pct Al alloy quenched from 975°C. In the composition range of 8 to 16 pct Al, where the alloys had been rolled about 25 pct reduction at 1000°C, annealing for 24 hr at 1000°C produced an equiaxed  $\alpha$  structure, as shown in Fig. 7. Alloys containing above 16 pct Al, which could not be fabricated, were examined after an homogenizing anneal of 24 hr at 1000°C. At 20 pct Al, Fig. 8, the structure consists of large Widmanstätten plates, indicative of a  $\beta$  to  $\alpha$  transformation structure. These plates probably existed in the as-cast alloy and were not overcome by the homogenizing anneal. Several cracks can be seen in the structures of the 16 and 20 pct Al alloys, illustrative of the inherent brittleness of the high aluminum-content  $\alpha$  range. At 25 and 26 pct Al, Fig. 9, equiaxed  $\alpha$  grain structures were obtained which showed no evidence of a transformation from the  $\beta$  phase. These data indicate that the solubility limit of aluminum in  $\beta$  titanium lies between 20 and 25 pct Al, probably quite close to 20 pct.

In the  $\alpha$ -plus- $\gamma$  field, the alloys have a banded

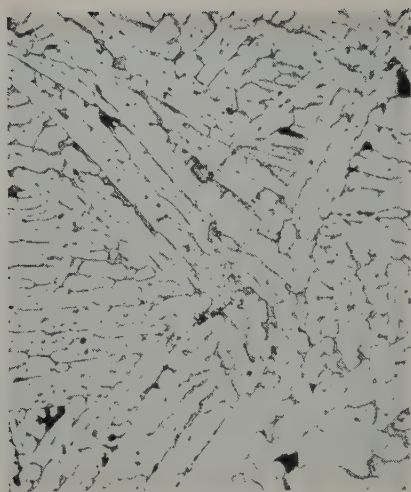


Fig. 16—Ti-72 pct Al alloy. X50.  
As-cast structure.  $TiAl_3$  and Al.

structure, suggesting that the  $\alpha$  phase has precipitated the  $\gamma$  phase on cooling. This is shown in the Ti-28 pct Al and Ti-30 pct Al alloys, Figs. 10 and 11, where the entire grain is banded. This indicates that the maximum solubility of aluminum in the  $\alpha$  phase is at least 30 pct at the  $\gamma$  peritectic temperature. At 32 pct Al, the banded structure still exists, but separate  $\gamma$  grains are beginning to appear. This structure is shown in Fig. 12.

Figs. 13 and 14 show microstructures of the  $\gamma$ -phase alloys after a homogenization treatment of 48 hr at 1100°C. The Ti-34 pct Al alloy has an equiaxed grain structure rather similar to that found in face-centered cubic metals. This structure persisted to 40 pct Al. From 42 through 46 pct Al, somewhat different structures, shown for the Ti-46 pct Al alloy in Fig. 11, were obtained. The fine structure shown there is not believed to be grain-boundary precipitation, but is more likely the result of coring derived from a long freezing range. If it is assumed that the composition of the  $\gamma$  phase at the peritectic temperature occurs at about 40 pct Al, then the differences in microstructure are readily understandable. A longer freezing range on the aluminum-rich side of this point could account for the heavily cored structure of these alloys.

The microstructure of a  $\gamma$ -plus- $TiAl_3$  alloy is shown in Fig. 15, and that of a  $TiAl_3$ -plus-aluminum alloy is shown in Fig. 16. The Ti-50 pct Al alloy consists of needles of  $TiAl_3$  in a matrix of  $\gamma$  phase, while the Ti-72 pct Al alloy consists of dendrites of  $TiAl_3$  with aluminum present as the dendritic filler. The  $TiAl_3$  phase has been identified in both of these alloys by X-ray diffraction using lattice spacings reported by Fink, Van Horn, and Budge.<sup>6</sup>

### X-Ray Diffraction

The lattice-constant curves showing the effect of aluminum on the lattice constants of titanium are given in Fig. 17. To obtain these data, powder samples of alloys containing up to 7.5 wt pct Al were heat treated for 1 hr at 800°C and alloys containing 10 to 25 wt pct Al were heat treated 20 min at 850°C. The lattice constant  $a_0$  decreases almost linearly with increasing aluminum content. However, the  $c_0$  curve shows a hump at low aluminum contents, which may be indicative of oxygen and/or nitrogen contamination in the powder samples. Clark<sup>7</sup> has shown that both oxygen and nitrogen cause an increase in the

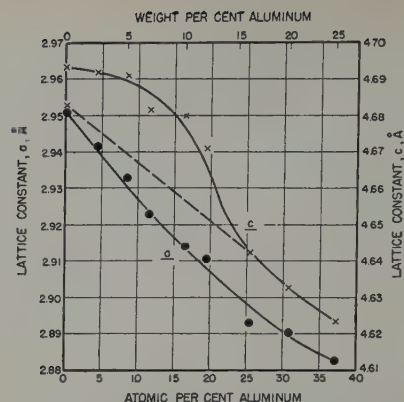


Fig. 17—Effect of aluminum on the lattice constants of titanium.

$c_0$  constant of titanium, but they do not significantly affect the  $a_0$  constant. However, even assuming some contamination of the low aluminum-content alloys, the  $c_0$  values in this range seem much higher than would be expected. Using the actual values, the axial ratio  $c/a$  increases almost linearly, 1.591 at 0 pct Al to 1.604 at 20 atomic pct Al. Above 20 atomic pct Al, the axial ratio remains constant at 1.604.

It was also found that the annealing treatment given to powder samples had a direct bearing on the lattice constants obtained. Filings of alloys containing 10 to 25 wt pct Al annealed in vacuum in the titanium-block holder for 24 hr at 1000°C had lattice constants corresponding to about 2.5 wt pct Al, and gave very diffuse patterns. This was probably caused by diffusion of the aluminum from the filings into the titanium capsule, or diffusion of titanium from the capsule into the filings. Similarly, powder samples of alloys containing 30, 35, and 40 wt pct Al, which had been identified microscopically as  $\alpha$ -plus- $\gamma$  and  $\gamma$ -phase alloys, had lattice constants of the  $\alpha$  phase corresponding to 2.5 pct Al with no  $\gamma$ -phase lines present when annealed 24 hr at 1100°C. These alloys were checked by X-ray diffraction examination of filings made from solid samples given the same annealing treatment. The patterns obtained were diffuse, because of the cold work present in the filings, but both the  $\gamma$  and  $\alpha$  phases could be identified in the 30 wt pct Al alloy and only the  $\gamma$  phase in the 35 and 40 wt pct alloys. Therefore, the technique of first homogenizing block samples of  $\alpha$ -plus- $\gamma$  and  $\gamma$ -phase alloys followed by low temperature annealing of the powder samples was adopted for these alloys.

Using the lattice-parameter curves in Fig. 17, an attempt was made to determine the effect of temperature on the solubility of aluminum in  $\alpha$  titanium.

Table III. Alpha Lattice Constants of a Ti-30 Pct Al Alloy Quenched from Various Temperatures

| Heat Treatment<br>(Water Quenched) |                      | Lattice<br>Constant, A* |       | Wt<br>Pct Al |
|------------------------------------|----------------------|-------------------------|-------|--------------|
| Time,<br>Hr                        | Tempera-<br>ture, °C | $a_0$                   | $c_0$ |              |
| 16                                 | 650                  | 2.884                   | 4.635 | 23 ± 1.5     |
| 8                                  | 750                  | 2.891                   | 4.637 | 20 ± 1.5     |
| 4                                  | 850                  | 2.887                   | 4.642 | 21.5 ± 1.5   |
| 1/2                                | 950                  | 2.887                   | 4.656 | 21.5 ± 1.5   |
| 1/4                                | 1050                 | 2.886                   | 4.632 | 22 ± 1.5     |

\* Degree of accuracy:  $a_0 \pm 0.003A$ ,  $c_0 \pm 0.007A$ .



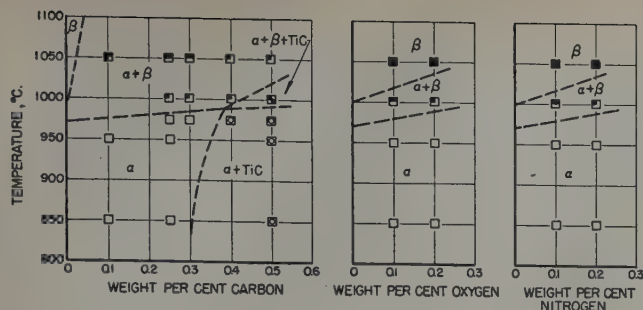


Fig. 18—Effect of carbon, oxygen, and nitrogen on the transformation range at the level of 5 pct Al.

Powder samples of a Ti-30 pct Al alloy were quenched from several temperatures, and lattice constants of the  $\alpha$  phase were determined. The lattice constants and corresponding aluminum solubilities at the various temperatures are given in Table III. The  $\alpha$  solubilities of aluminum calculated from the X-ray diffraction data are of the same order of magnitude but are 2 to 3 wt pct Al lower than the value determined microscopically. The lower solubilities are believed to be caused by the diffusion effect noted before. Therefore, it is considered that the metallographic observations on the terminal solubility of aluminum in  $\alpha$  titanium are more reliable than those using X-ray diffraction.

Diffraction patterns of  $\gamma$ -phase alloys (33 to 46 wt pct Al) were diffuse, and precision lattice constants could not be obtained. Filings for this work were taken from block samples homogenized for 48 hr at 1100°C and then given a short-time strain-relief anneal. The diffuse patterns may have been caused by either an insufficient homogenization treatment, or an insufficient strain-relief anneal. However, good patterns were obtained of the  $\gamma$  phase from alloys in the  $\alpha$ -plus- $\gamma$  and  $\gamma$ -plus  $\text{TiAl}_3$  fields, so that the lattice constants of the upper and lower limits were obtained. These are given in Table IV. The crystal structure has been established as face-centered tetragonal with an axial ratio  $c/a$  of 1.012 to 1.018. It is interesting to note that the lattice constants of the  $\gamma$  phase are very close to the lattice constant of aluminum, 4.0408Å.<sup>8</sup> It has also been established that the  $\gamma$  phase has an ordered structure, probably of the CuAu type with alternate layers of titanium and aluminum atoms. Superlattice lines were observed in all alloys containing from 30 to 50 wt pct Al, and, although precision lattice constants could not be determined for  $\gamma$ -phase alloys, the superlattice lines were still discernible. Quenching alloys containing 35 to 40 wt pct Al from temperatures up to 1050°C did not overcome the ordered structure, indicating either that no order-disorder transformation exists at least up to 1050°C, or that it cannot be suppressed by quenching.

### Effects of Carbon, Oxygen, and Nitrogen

Because carbon, oxygen, and nitrogen are the major impurities present in commercial grades of

Table IV. Lattice Constants of Gamma Phase

| Aluminum Content |            | Lattice Constants, Å |        | Other Phases Present |
|------------------|------------|----------------------|--------|----------------------|
| Wt Pct           | Atomic Pct | $a$                  | $c$    |                      |
| 30               | 43.25      | 4.0155               | 4.0625 | $\alpha$             |
| 50               | 64         | 3.976                | 4.049  | $\text{TiAl}_3$      |

titanium, it is important to know their effects in small quantities on the Ti-Al diagram. Fig. 18 shows the effect of carbon, oxygen, and nitrogen on the transformation range at the 5 pct Al level. All three of the interstitial additions raise the  $\alpha$  and  $\beta$  transus temperatures markedly, which is what might be expected from the previous data on the binary alloys of these elements with titanium.<sup>4</sup> In all three cases, the slopes of the  $\alpha$  and  $\beta$  transus lines have been estimated from the quantity of  $\beta$  present at temperatures within the  $\alpha$ - $\beta$  field. Precise determinations of the exact location of these lines have not been made.

### Summary

The titanium-rich portion of the Ti-Al diagram has been surveyed between room temperature and 1100°C. Very limited data were taken above 1100°C, and the diagram in this region has been sketched in chiefly to conform with melting point data and microstructural appearance of cast alloys. The main features of the diagram may be summarized as:

1—The solubility of aluminum in  $\alpha$  titanium is about 26 wt pct.

2—The temperature of  $\alpha$  to  $\beta$  transformation is increased by aluminum additions, resulting in a two-phase field where  $\beta$  solubilities are less than  $\alpha$  solubilities. This is the first documented case of a metallic  $\alpha$ -stabilizing addition for titanium.

3—A new phase designated as  $\gamma$  occurs between 34 and 46 pct Al. This phase has an ordered face-centered tetragonal structure with an axial ratio close to unity and with lattice constants very close to the lattice constant of aluminum.

4—Aluminum additions up to 20 pct do not appreciably lower the melting point of titanium. Above 20 pct Al, the melting point is markedly lowered.

In addition, the effects of small amounts of carbon, oxygen, and nitrogen on the transformation range of Ti-Al alloys have been surveyed.

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# Model for Dendrite Growth Form in Metals and Alloys

by R. B. Pond and S. W. Kessler

Metal specimens were solidified through a measured thermal gradient so a free surface and the liquid-solid interface could be examined. A line structure was observed on the surface and a hexagonal structure on the interface. A model to explain these forms is proposed.

NUMEROUS observations of the dendrite form have been made both in nonmetallic and metallic systems. From these, extrapolations have been made as to the probable dendrite form in pure metals. Observations of the dendrite form in pure metals, nevertheless, have been scanty. In general, these observations have been made on the skeleton dendrite after the mother liquid has been drained from around it, and a mechanism of the formation of the dendrite has been postulated from this solid form. Recent investigations have been conducted in an endeavor to make a study of the formation of the dendrite in several pure metals and the effect of several variables on this mechanism and final form. For these investigations, an apparatus was designed and constructed as shown in Fig. 1. It consists of a talc block containing a half-cylindrical depression, the end of which terminates in the conical recess of a copper block having an external attachment for cooling. A heating coil extends the length of the mold just beneath the lower limits of the cavity. The entire cavity for holding metal is coated with a thin film of graphite. Six thermocouples are equally spaced in the cavity and under the graphite, and six microammeters indicate the temperatures at the particular thermocouple stations. Readings were taken of all meters at the same instant time measurements were taken by photographing the panel of microammeters and a stop watch which was started at the beginning of the run.

It was possible with this apparatus to solidify metals through a measured thermal gradient and to observe the progression of the liquid-solid interface with time by following the formation of the dendrite markings in the surface of the solid material. These

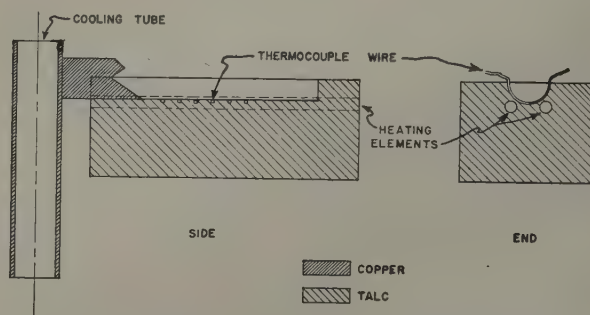


Fig. 1—Schematic drawing of mold used in studies of growth form.

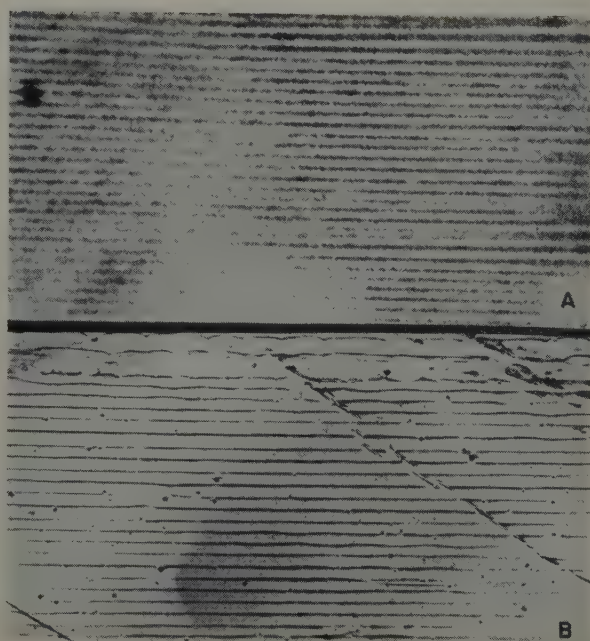


Fig. 2A—Reproduction of Graf's picture<sup>2</sup> of layer structure in copper. Estimated X1000. B—Longitudinal striae in pure indium. X450.

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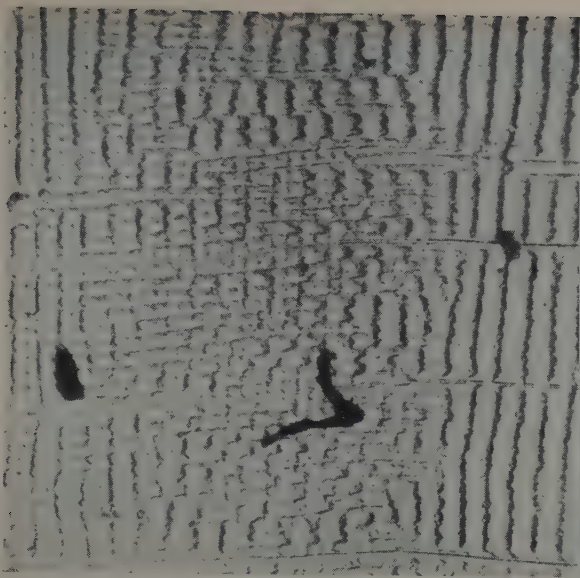


Fig. 3—Typical longitudinal and transverse striae witnessed in the surface of solidified pure tin. X50.

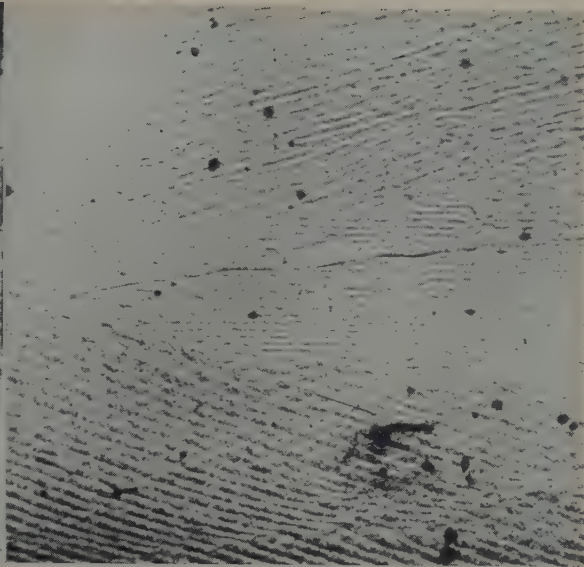


Fig. 4—Longitudinal striae delineating grain boundaries in pure tin. X50.

dendrite markings apparently were caused by the unequal and progressive growth of the dendrite segments and shrinkage of the liquid between these segments. When the residual liquid solidified, it was at this new level; and the dendrite was then marked out in relief. The dendrite in relief gave a frosted appearance to the solid as described by Turnbull and Cech,<sup>1</sup> while the liquid maintained a shiny mirror-like surface.

During the course of investigation, it was desired to observe the shape of the total liquid-solid interface in order to determine if the surface trace was characteristic of the total interface. This was accomplished by sucking the metal from the molten part of the bath at an extremely rapid rate after partial solidification. This process allowed another view of the dendrite form which was witnessed on the surface.

The dendrite form as witnessed on the surface was a stria or line structure aligned parallel, or roughly parallel, to the direction of growth (longitudinal striae), as well as a coarser line structure which was aligned roughly perpendicular to the longitudinal striae (transverse striae). The longitudinal striae were observed to be almost identical in form with that structure reported by Graf<sup>2</sup> as a layer-type structure, as can be seen in Fig. 2 by comparing his structure with the longitudinal striae. The transverse striae were not so easily witnessed and proved most difficult to photograph at the same time as the longitudinal striae. Fig. 3 shows the presence of both striae, and Fig. 4 shows the predominant appearance of the longitudinal striae and their delineation of the grain boundaries. The transverse striae in Fig. 4 appear only by faint light bands across the structure.

The longitudinal striae are of crystallographic origin, i.e., parallel within each grain but different from grain to grain. The transverse striae, on the other hand, often would be found to be parallel across all grains. It has been shown that this transverse striae is not a true dendrite marking however, but is a shrinkage mark. This is explained with reference to Fig. 5. If the original volume of material  $S + L$  is liquid and solidification proceeds from 1 to 5, the first volume of material to solidify at 1 will be

at the liquid level, A. As the rest of the material decreases in temperature, the liquid level drops to B; and as the volume of material 2 solidifies, it will be at level B. This process is repeated, thereby giving a step-like surface to the solid, S, which will show as striae when viewed from above. This model points to the fact that the transverse striae should be more prominent in portions of the specimens where the liquid-solid interface existed when the liquid solidified under the most rapid rate of cooling. This was found to be the case. Fig. 6 is a micrograph of polycrystalline pure tin which was solidified from a point source and shows the transverse marking as arcs emanating from this point. Since these marks have a definite curvature in each grain, they cannot be classed as crystallographic or dendritic markings.

The bled face showed a hexagonal network similar to the hexagonaloid structure shown by Buerger.<sup>3</sup> Fig. 7 indicates that the longitudinal striae is the impression of the tops of the hexagons in the surface. A higher magnification of this structure shows a characteristic array of almost perfect hexagons, cf. Fig. 8. Fig. 9 shows the hexagonaloid to be a three dimensional unit with a breastlike shape; consequently, the name mammiform is assigned to it since this is the noun form of the word given by Dana<sup>4</sup> to describe such imitative shapes. A check to determine if these forms represented different grains was made by examination under polarized light. Fig. 10 shows three grains, each containing mammiforms, the grain boundaries being mammiform boundaries, and shows the mammiform in any one grain to be consistent in orientation with the rest of the grain. The specimen was deformed to produce twin bands which can be seen crossing the mammiforms and terminating at

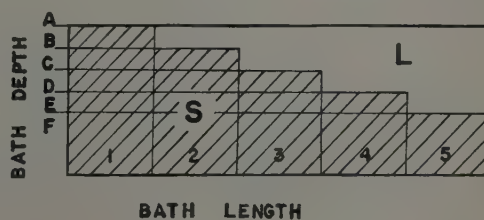


Fig. 5—Schematic sketch of step-like solidification.





Fig. 6—Transverse striae showing as circular marks in pure tin. X40.

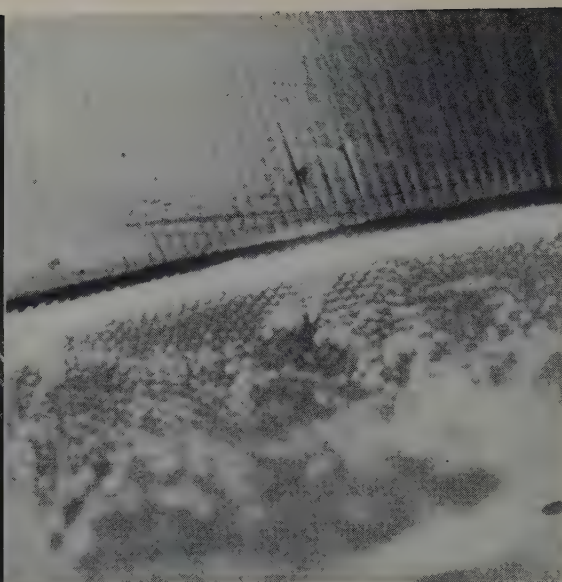


Fig. 7—Billet of pure indium showing the correlation of the mammiforms in the bled face with the longitudinal striae in the surface. Approximately X15.

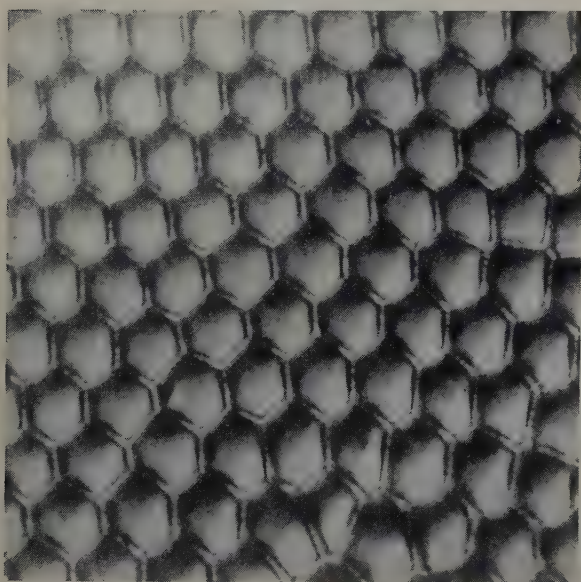


Fig. 8—Ends of the longitudinal striae in pure tin showing the characteristic hexagonal array. X125.

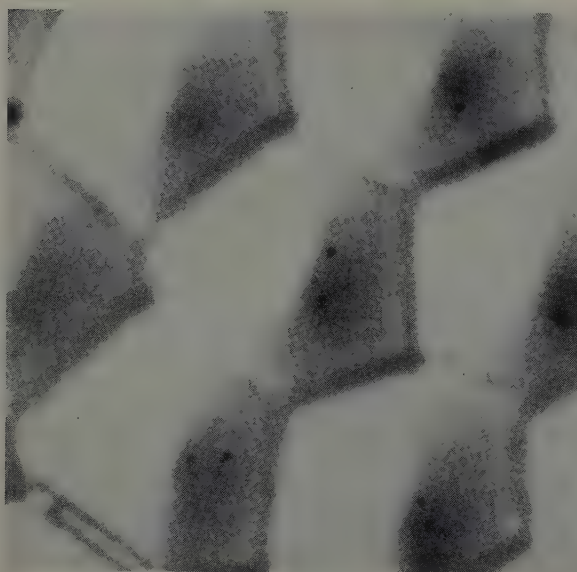


Fig. 9—Typical three dimensional structure of the mammiform in pure indium. X400.

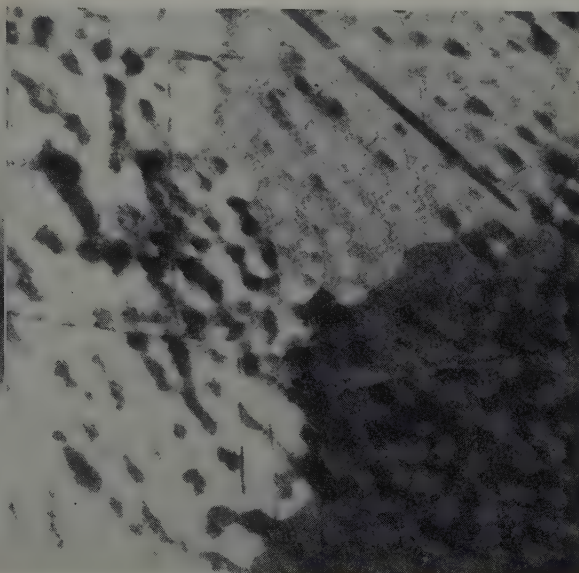


Fig. 10—Grain boundaries in pure tin portrayed under polarized light follow mammiform boundaries. X50.

the grain boundaries. It is to be noted that this structure is not the same as the cellular structures reported by Bengough,<sup>7</sup> and referred to as a double ture, the formation of which is described by Desch.<sup>6</sup> The cells of these structures are individual grains. The observed structure is probably the same as that reported by Bengough,<sup>7</sup> and referred to as a double cellular network, as well as by Smialowski<sup>8</sup> and Buerger.<sup>8</sup>

In an attempt to explain the hexagonal shape of the rod of the dendritic structure, consider an array of identical cones situated on a plane so that the axes of the cones are perpendicular to the plane, and are in a close-packed arrangement. If the cones are made sufficiently large so that their sides will everywhere intersect the sides of neighboring cones, these intersections will describe a net of hexagons,



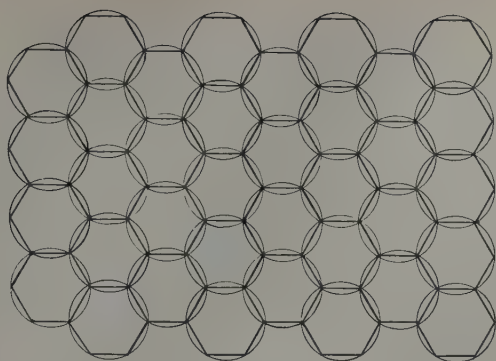


Fig. 11—Development of array of hexagons by the intersection of cone bases.

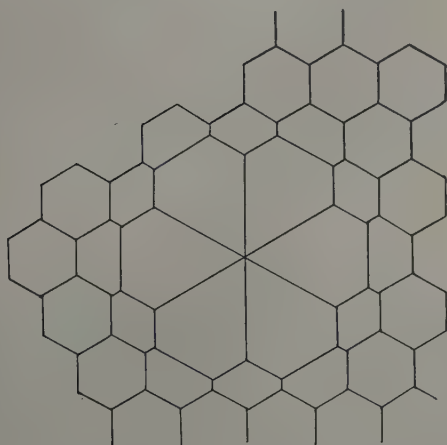


Fig. 12—Sharp nosed pentagons developed by omitting one cone from the array.

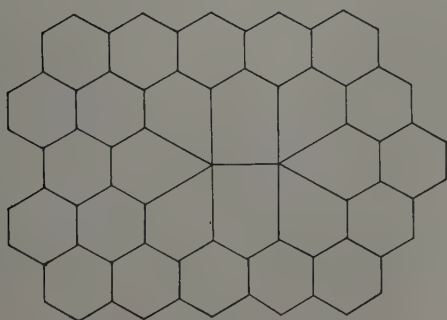


Fig. 13—Square nosed pentagons developed by omitting two cones from the array.

cf. Fig. 11. It should be noted in Fig. 8 that there are other than six-sided figures. Using the model shown in Fig. 11, the misshapen figures can be explained by omitting a selected nucleus from the structure. Fig. 12 illustrates sharp-nosed pentagons obtained by omitting one nucleus, and Fig. 13 indicates square-nosed pentagons obtained by omission of two nuclei. Mammiforms were also observed where no great uniformity of shape existed, as in Fig. 14. Such nonuniform shapes can be constructed by omission of a sufficient number of selected nuclei.

Two major explanations are necessary relative to the inherent hexagonal shape of the rods. One, by what mechanism is the hexagonal close-packed

site selected for growth of the mammiforms; and two, why the particular shape of the mammiform? In an endeavor to answer the first question reference is made to Fig. 15.

The assumption is made that the block of material XYZ is solid material which has been solidified from the melt, and in which the face X represents the liquid-solid interface. The control gradient (or the gradient which controls the flow of heat from the liquid) along this block of material is expressed by line 1 and the solidification temperature of the material by line 2 on the temperature-distance curve adjacent to the block material. It will be noted that the temperature at the interface in this static condition is the solidification temperature of the metal. It is assumed, for the moment, that a block of material of mass A adjoins itself to the solid structure at A and transforms from a liquid into a solid. The latent heat of fusion of this mass A may be given up in three ways: 1—It may be conducted into the already solid material in accordance with the control gradient. 2—It may be diffused into the liquid in accordance with the temperature gradient in the liquid and the conductivity of the liquid. 3—It may be diffused in the surface X toward the boundaries of this face.

The thermal diffusivity of the metal in the surface X will determine the rate at which this heat is conducted away from point A. Consider, now, the heat dispersion in plane X at time  $t_1$ . For simplicity's sake, plane X is assumed to be thermally isotropic. It will be noted that the temperature at point A has been increased to  $A_1$ , as shown on the temperature-distance curve. If the mass A is to remain solid at the temperature  $A_1$ , either the small solid particle can be heated to  $A_1$  without melting, or  $A_1$  is the true solidification temperature and supercooling to the noted solidification temperature curve 2 is necessary to cause this initial solidification. The surface thermal gradient from point  $A_1$  is expressed by curve 3, and that closest point at which another mass of material can solidify is to be found on that loci of points represented by the surface gradient curve 3 crossing the solidification temperature curve 2. If it is now assumed that solidification occurs at some random point B of this loci of points, the latent

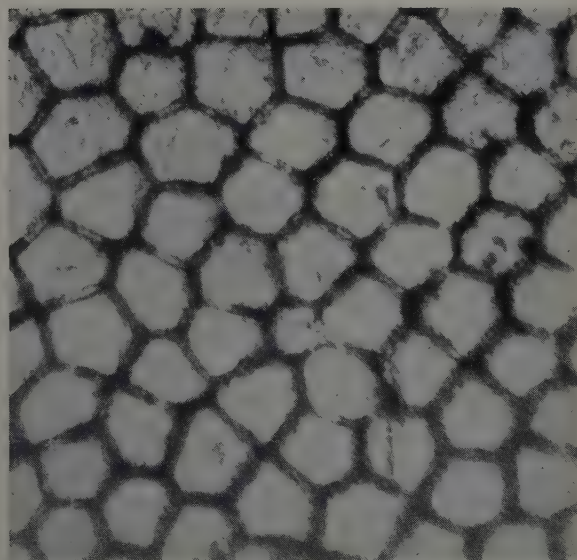


Fig. 14—Mammiforms in pure lead showing no extensive uniformity of shape. X50.

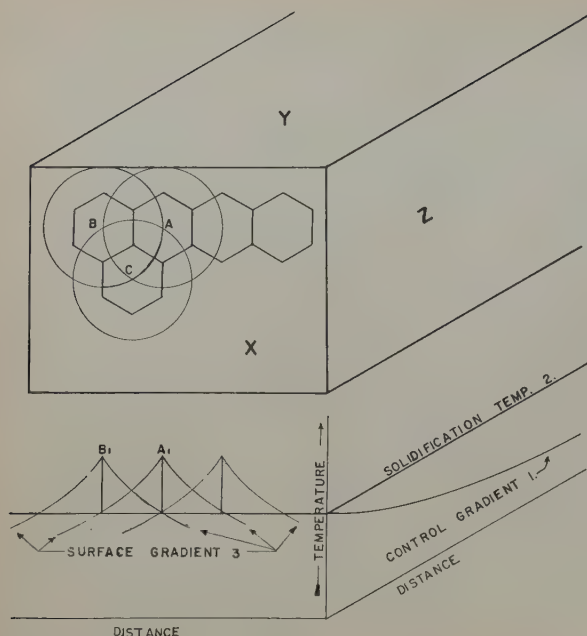


Fig. 15—Model for explaining mammiform site selection.

heat of fusion as noted before for A will be dispersed in a like manner; and a new loci of points will exist at which another mass of material can solidify. The possible positions of solidification determined by mass A are still imposed. The closest approach to A and B for this newest point will be at C, assuming that there is a proper balance of heat flow in the surface gradient and the control gradient. It is noticed that these A, B, and C points are in a close-packed arrangement, or that the angles between lines connecting these points are  $60^\circ$ . If, however, the balance of heat flow in the surface gradient and control gradient are not properly adjusted, point C may be removed away from points A and B or toward points A and B, thereby increasing or decreasing the closeness of packing.

If the solidification of masses A, B, and C should occur simultaneously and in a random fashion, so that any one mass is within the surface control gradient of another mass, then one of the masses must liquefy, since it will be above the solidification temperature. Consequently, the simultaneity of solidification is improbable unless the control gradient is sufficiently steep so that heat is removed from all masses at a rate such that the surface control gradient areas are very small. In this case, the masses may be solidified in random distribution. It should

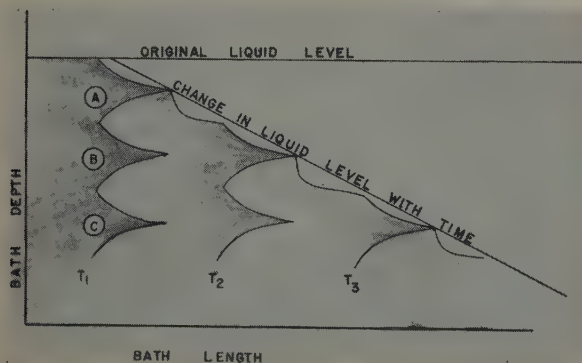


Fig. 16—Model for explaining step-like solidification.

be noted that if the entire surface X is at the temperature of solidification, the deposition process may start from a multiplicity of points; and that although a close-packed array may exist in each area, the zones between these areas need not show a continuance of the order.

With this model for the selection of growth sites and the accompanying order of growth sites, there will be growth from these points in accordance with the growth vectors of the materials being solidified; i.e., the shape of the liquid-solid interface will be determined by the orientation of the crystal. However, this shape will be determined for every growth site, and consequently the liquid-solid interface for each site will approximate a cone projecting into the liquid if growth proceeds in a symmetry direction. Since the cone projected into the liquid will be entering areas of different temperature, or since a temperature gradient will exist down the axis of the cone, the shape of the cone cannot be expected to be extremely regular; and it will more nearly approach a mammiform structure. If this particular shape has grown out from the original plane X, a time will be reached when the bases of these mammiform figures will intersect. These intersections will form hexagons if the sites are in close-packed array. If the site C is removed from sites A

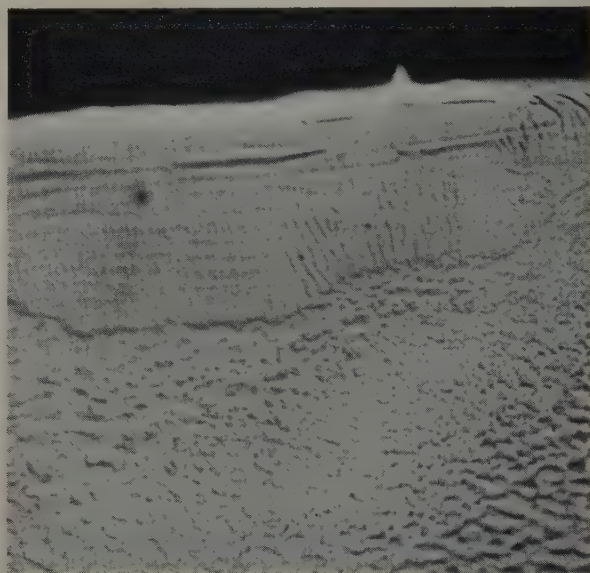


Fig. 17—Liquid-solid interface in pure tin which was not progressing when liquid was sucked off. Note absence of mammiforms. X500.

and B, as previously described, the shape of the intersection figures will be flattened hexagons. If a mass site is erased by being situated too close to another site, as described above, and yet exerts its influence on a third site prior to its eradication, then a vacant site may exist and the figures in this locale will be irregular pentagons, cf. Fig. 12. If the two sites are so erased, there will be two zones of irregular pentagons of different shapes. By making various sites disappear, almost any type figure can be made to exist, cf. Fig. 13, or if the sites are laid down at random as may occur if the control gradient is sufficiently steep, the figures will present themselves in many devious designs.

If growth from one site occurs before growth from other sites due to local differences in the control thermal gradient, then the size of the particular fig-



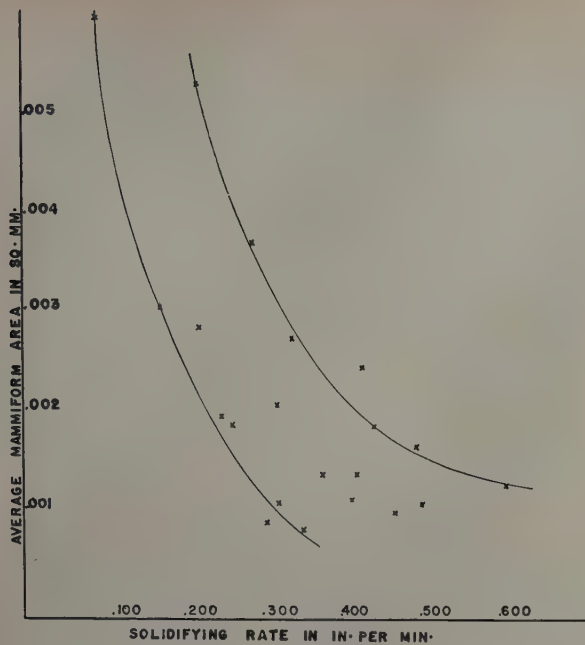


Fig. 18—Plot of average mammi-form size vs. solidification rate.

ure around this site will be relatively larger than its neighbor; but its geometry will remain unchanged. Conversely, a site which is delayed in its growth will have a relatively small size, and its geometry will be changed, cf. Fig. 12.

The transverse markings might be formed by the following mechanism: In Fig. 16, the original liquid level and the change in liquid level with time are represented at various positions of the bath; a series of mammi-forms A, B, C, etc., are growing; and at time  $t_1$ , the tip of mammi-form A has reached the liquid level and cannot propagate further into the liquid. The upper side of the form will continue to grow as long as there is metal available to feed it;

but it must be remembered that the liquid can flow off around the sides of the form, and consequently it will never be able to utilize the entire volume of metal available to it at  $t_1$ . The lower side of the form will also continue to grow until it grows out of the liquid so that at  $t_2$ , the tip of mammi-form B will have reached the liquid surface and mammi-form A will have terminated its growth in the profile shown. As the mammi-forms A, B, C, etc., continue to follow this procedure, the step-like shrinkage marking, previously described, is developed.

In the above models, the mammi-form is a growth form and would not be present if growth were not proceeding. The liquid-solid interface was held in one position for an hour by establishing a steady-state condition of heat flow and then all of the liquid was sucked off. No mammi-forms could be observed, as seen in Fig. 17. The background structure may be explained by the rapid solidification of that liquid metal which was wetting the solid metal and which could not be drawn off. Near the top edge of the specimen where drainage was more complete, an

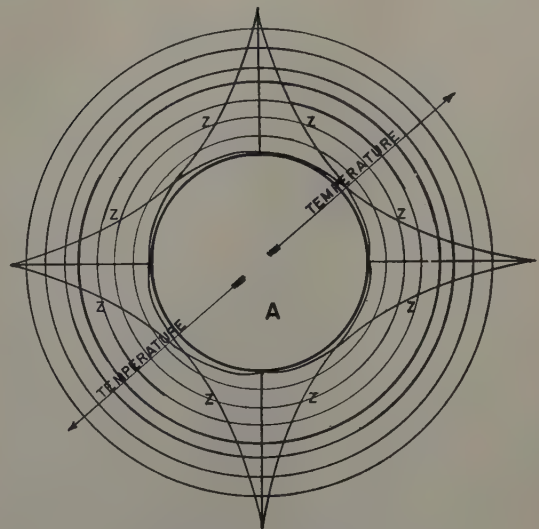


Fig. 20—Model for explaining radial distribution of dendrite arms.

absence of this fine structure may be noted. This experiment was repeated with the exception that after the interface had been stopped for an hour growth was allowed to continue and the liquid immediately sucked off. The characteristic mammi-form structure was found.

By the above model, it was speculated that the steeper the control gradient in the solid, the greater would be the quantity of heat conducted into the solid per unit time and the smaller would be the available heat from the nucleus to be distributed in the liquid-solid interface. This means that the area influenced by a nucleating mass will be smaller or that the base area of the mammi-form would be smaller. Since the steepness of the control gradient was found to be roughly proportional to the rate of solidification, the average mammi-form sizes in specimens which had been solidified at various rates were determined and plotted vs. rate of solidification, Fig. 18. The envelope including the points shows the tendency for decrease in mammi-form size with an increase in growth rate as predicted from the proposed model.

Since the first observations and investigations of the mammi-form were made in specimens produced

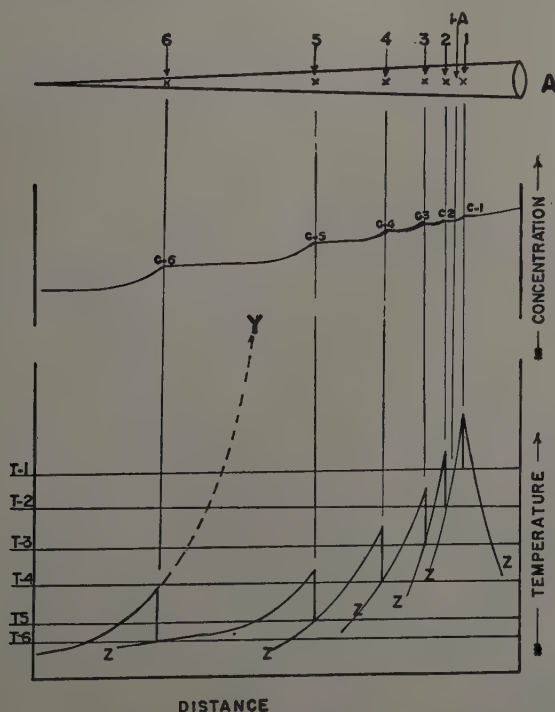


Fig. 19—Model for explaining the tree-like dendrite of solid-solution alloys.

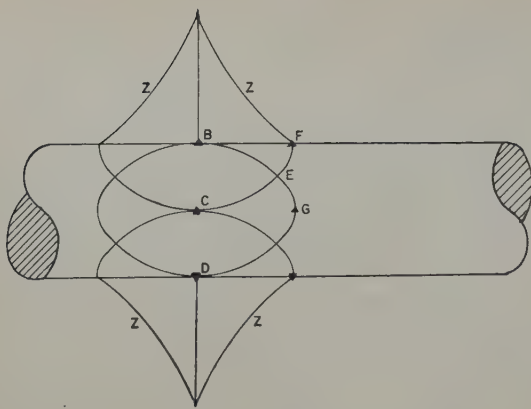


Fig. 21—Model for explaining alignment of mammiform sites along axis of original form.

as described above, it seemed necessary to check the existence of the mammiform when the metal was solidified in other ways. Polycrystalline metal masses were solidified in deep and shallow pots from the bottom, and in hollow tubes from the outside. In every instance, mammiforms were witnessed. The mammiforms were observed in all metals investigated, i.e., 99.997 pct pure Sn, 99.99+ pct pure Pb, 99.998 pct pure Bi, 99.999 pct pure In, 99.8+ pct pure Sb, and 99.997 pct pure Al.

An application of the proposed mammiform model in the case of the solid-solution alloys may be made in an endeavor to explain the mechanism of formation of the tree-like dendrite form. This is done by the imposition of a concentration gradient on the model, Fig. 19. The assumption is made that a relatively long mammiform A has grown onto the liquid-solid interface, that the temperature of the surface of this mammiform is (over microscopic segments) constant, and that with a given core temperature of the mammiform, the thermal gradient curve of this material is represented as curve Y. If a mass of concentration c-1 of solidification temperature T-1 deposits on site 1, the local temperature will be increased and the surface temperature gradient Z will be established so that the closest approach of the next mass c-1 to be deposited will be at 1-A. However, with reference to the concentration curve, it is seen that the concentration at point 1-A is c-2 and its solidification temperature T-2 and a solid mass of c-2 will not deposit at 1-A. However, at site 2 the solidification temperature T-2 has been reached and so c-2 will deposit there. The latent heat of fusion of c-2 will be given up and the process repeated. Since the temperature achieved by mass c-2 is less than that attained by c-1, the slope of the thermal gradient curve is less and so the site 3 where c-3 will deposit will be further from site 2 than site 2 is from site 1. This indicates that as growth proceeds, the concentration is changed, longer time is required for solidification because of the decrease in the temperature difference between the mammiform core temperature and the site temperature, and the cross arms should get farther and farther apart. This variation of distance between dendrite cross arms and speed of solidification as dependent on progression of growth was noted by Alexander and Rhines.<sup>9</sup> They also noted that the dendrite spacing in any one alloy system varied in the same manner as the ratio of the heat of fusion to the thermal diffusivity. In the proposed model, it is noted that the

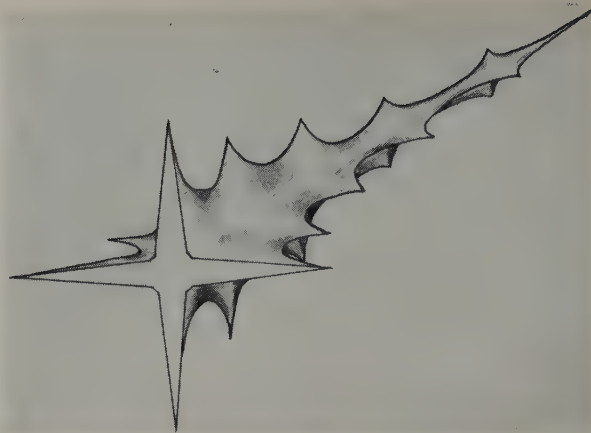


Fig. 22—Schematic drawing of growth of the mammiform bases together to form webs.

slope of the surface control gradient curve Z, which determines the closeness of approach of the dendrite arms, will vary directly with the latent heat of fusion of the metal being deposited and inversely with the thermal diffusivity of the metal already deposited.

Reference to the probable temperature distribution curves Z around the mammiform, Fig. 20, indicates that the mammiform sites will be distributed 90° around the original mammiform. Fig. 21 shows how the mammiform sites are maintained in alignment along the length of the original form. After the masses B, C, and D, Fig. 21, have been deposited, it appears that E would be the next site to be occupied. However, the solute element has been diffusing toward E from both B and C, and point E will therefore be replete in the solute and have a lower solidification temperature than either G or F, so the points G and F will be selected as mammiform sites prior to E. As the mammiforms are continually formed in a line parallel to the original mammiform axis, their bases will grow together to form a web between the forms, Fig. 22. Cross arms on the cross arms can be developed in the same manner.

### Acknowledgment

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# A Survey of the Sulphur Problem Through The Various Operations in the Steel Plant

by T. E. Brower and B. M. Larsen

A perspective is presented of the steel plant sulphur distribution and elimination problem from coal to liquid steel ready for teeming, giving distributions of sulphur over a range of coke sulphur content, and some methods of sulphur control, in the blast furnace, external desulphurization between blast furnace and open hearth, distribution between fuel, slag, and metal, and methods and limitations of control of sulphur in the open hearth furnace.

AS a part of the 1951 AIME symposium on sulphur in steelmaking, it was thought that a discussion of the distribution of sulphur throughout the whole series of operations, from coal and ore to finished steel ingots, might have some value in giving a perspective on the whole problem. The following discussion is an attempt to present such an overall picture. The order is that of the actual plant operations, beginning with a very brief consideration of the coking process.

## Sulphur in Coal and Coke

Since by far the largest source of sulphur entering the steelmaking cycle is in the coal used to make coke for the blast furnace, it would seem reasonable to eliminate some of it, either from the coal, or the coke, or during the coking process. This has appeared impracticable up to the present, at least, for two main reasons: the low activity of the organic sulphur in either coal or coke, and because of price limitations involved in treating a low cost material such as coke.

A variable portion, usually  $\frac{1}{2}$  or less, of the sulphur is present in coal in the form of pyrites or similar compounds, and a large part of this sulphur may be removed in the coal washery. Most of the sulphur, however, is normally present as "organic" sulphur, intimately associated with the coal structure. Its distribution prevents any separation by mechanical means. Its low activity makes improbable any rapid chemical removal, although hydrogen will remove sulphur from both coal and coke. Thus, prolonged recirculation of coke oven gas in the coking process would tend to leave a smaller percentage of the total sulphur in the coke residue. Table I shows a typical distribution of sulphur from coal into products in the coking process. As the sulphur in the coal increases, the sulphur in the coke tends to increase in about the same proportion.

## Sulphur in the Blast Furnace

The best picture of the situation in the blast furnace is provided by a sulphur balance of raw materials entering, and of products leaving, the furnace. The difficulties in accurate weighing and sampling

of the variable solid materials entering this process, and the number of hours required for the raw materials to descend through the furnace under variable operating conditions, make it difficult to obtain an accurate balance. However, balances made over periods of weeks or months tend to average out some of these uncertainties.

Table II presents three typical sulphur balances similar to a number that the writers have calculated. In most of these the slag volume calculated from the sulphur balance is, in some instances more, and in other instances less, than the value corresponding to the best input and output balances of the other slag constituents (lime, silica, alumina, etc.). Probably the greatest source of error in these calculations is the sulphur content of the slag. Despite some possible inaccuracies the balances of Table II show rather definitely the following points:

1—That 87 to 95 pct of the total sulphur input is in the coke and 95 to 97 pct of the total sulphur output is in the slag. Also, that if any sulphur leaves the furnace with the gas it is relatively small, amounting to a possible 1 pct or less.

2—At the lower sulphur coke level of 0.86 pct the total amount of sulphur charged is 15 lb of sulphur per ton iron increasing to 26 lb per ton at the higher sulphur, intimately associated with the coal structure burdens containing sulphur-rich ores will the total sulphur burden fail to be nearly proportional to the content in the coke used.

3—The 7 to 9 pct of the total sulphur input from the limestone of furnaces B and C is due to the relatively high sulphur content of the stone, 0.226 and 0.265 pct, respectively. In the case of furnace A, the sulphur content of the limestone was only 0.06 pct which resulted in only 3 pct of the total sulphur input coming from this source.

It is rather interesting to compare the sulphur balances of a typical ferromanganese furnace with

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Table I. Distribution of Sulphur from Coal During the Coking Process

| Coal,<br>Pct S | Lb S<br>per<br>Ton<br>Coal | Coke,<br>Pct S | Lb S<br>per<br>Ton<br>Coal | Gas,<br>Grains<br>S per<br>per 100<br>Cu Ft | Lb S<br>per<br>Ton<br>Coal | Tar,<br>Pct S | Lb S<br>per<br>Ton<br>Coal |
|----------------|----------------------------|----------------|----------------------------|---------------------------------------------|----------------------------|---------------|----------------------------|
| 0.80           | 16                         | 0.56           | 8.1                        | 240                                         | 2.9                        | 0.40          | 0.6                        |
| 1.20           | 24                         | 0.87           | 12.5                       | 420                                         | 5.0                        | 0.61          | 0.9                        |
| 1.60           | 32                         | 1.15           | 16.6                       | 600                                         | 7.2                        | 0.81          | 1.2                        |

the iron furnaces of Table II. Briefly the comparisons are as follows:

1—The percentage distribution of the items of the total sulphur input of both types of ore smelting is practically identical. That is, in the ferromanganese furnace 92 to 94 pct of the total sulphur is in the coke. Since the coke consumption of the ferromanganese furnace is approximately double that of the iron furnace, the total sulphur input is in the neighborhood of 40 to 45 lb sulphur per ton of ferromanganese for a 1.06 pct sulphur coke. (Compare with the iron furnace B of Table II which has a total input of 20.5 lb sulphur per ton iron.)

2—The output side of the sulphur balance of the two smelting processes is somewhat different. In the case of manganese smelting about 1 pct or less of the total sulphur is in the ferromanganese and approximately 80 to 85 pct is in the slag. The remaining 14 to 19 pct of the total sulphur was probably carried in the fine fume passing out the top of the furnace.

Since nearly all the sulphur burden in iron smelting can be attributed to the coke, the sulphur content of this raw material becomes of prime importance. In this country, coke with relatively low sulphur contents (0.70 to 1.00 pct) is becoming less common; we are having more and more to use cokes containing normally 1.20 and 1.30 pct, with periods of wide variations which occasionally reach values as high as 1.80 and 2.00 pct.

Table II. Sulphur Balance of Blast Furnaces Over One Month's Operation

| Item                      | A<br>Coke S =<br>0.86 Pct  |                      | B<br>Coke S =<br>1.08 Pct  |                      | C<br>Coke S =<br>1.42 Pct  |                         |
|---------------------------|----------------------------|----------------------|----------------------------|----------------------|----------------------------|-------------------------|
|                           | Lb<br>S per<br>Ton<br>Iron | Pct of<br>Total<br>S | Lb<br>S per<br>Ton<br>Iron | Pct of<br>Total<br>S | Lb<br>S per<br>Ton<br>Iron | Pct<br>of<br>Total<br>S |
| Input                     |                            |                      |                            |                      |                            |                         |
| Coke                      | 14.18                      | 94.1                 | 18.12                      | 88.3                 | 23.45                      | 89.8                    |
| Limestone and<br>dolomite | 0.45                       | 3.0                  | 1.76                       | 8.6                  | 1.79                       | 6.9                     |
| O.H. slag                 |                            |                      | 0.26                       | 1.3                  | 0.39                       | 1.5                     |
| Ore, sinter               | 0.39                       | 2.6                  | 0.37                       | 1.8                  | 0.45                       | 1.7                     |
| Scale and scrap           | 0.05                       | 0.3                  |                            |                      | 0.04                       | 0.1                     |
| Total                     | 15.07                      | 100.0                | 20.51                      | 100.0                | 26.12                      | 100.0                   |
| Output                    |                            |                      |                            |                      |                            |                         |
| Flue dust                 | 0.08                       | 0.5                  | 0.11                       | 0.5                  | 0.27                       | 1.0                     |
| Iron                      | 0.48                       | 3.2                  | 0.66                       | 3.2                  | 0.84                       | 3.2                     |
| Slag                      | 14.51                      | 96.3                 | 19.74                      | 96.3                 | 25.01                      | 95.8                    |
| Total                     | 15.07                      | 100.0                | 20.51                      | 100.0                | 26.12                      | 100.0                   |

Sulphur distribution as determined by slag volume, calculated from other materials balances, is as follows:

|                                        |       |      |              |      |  |
|----------------------------------------|-------|------|--------------|------|--|
| CaO Balance                            |       |      |              |      |  |
| S in slag                              | 14.43 | 95.8 | 20.46        | 96.4 |  |
| S unaccounted for                      | 0.08  | 0.5  | -0.72        | 3.4  |  |
|                                        |       |      | (input side) |      |  |
| Al <sub>2</sub> O <sub>3</sub> Balance |       |      |              |      |  |
| S in slag                              | 14.14 | 93.8 | 19.37        | 94.4 |  |
| S unaccounted for                      | 0.37  | 2.5  | 0.37         | 1.8  |  |
| Average pct S in<br>slag               |       | 1.74 | 2.01         | 2.49 |  |

Accordingly the sulphur problem of the blast furnace becomes one of distributing the total sulphur input between slag and iron so as to leave the iron with minimum sulphur content. Obviously this becomes more and more important as the total input increases due to the necessary usage of higher sulphur cokes.

With a process capable of leaving only about 3 pct of its total sulphur burden in the iron produced, desulphurization in the blast furnace is a problem only because the open hearth has such a limited capacity for sulphur removal. This is illustrated by the sulphur balances of the open hearth which will be discussed in more detail later. It is sufficient to mention that this small amount of sulphur remaining in the iron usually becomes, in turn, the largest single item of the sulphur input to the open hearth furnace. The slag-metal distribution follows the simple distribution law, not exactly perhaps, but closely enough to serve as a good guide in practice. That is, if the total sulphur input is doubled, the percentages in both slag and metal will be approximately twice as large. Since measured distribution ratios of sulphur in slag to sulphur in metal ( S )/[S ] vary from about 15 to 150, it would seem possible to compensate for a large increase in total sulphur burden, but there are limitations in practice:

Increasing the slag volume also increases the coke consumption, which, in addition to lowering production rate, causes the effect to be partially offset by the accompanying increase in total sulphur, since most of this comes from the coke. According to Steudel<sup>1</sup> each increment of 100 lb of slag requires approximately 50 lb of extra coke. This estimate agrees with that indicated by differences which existed in former years between northern and southern blast furnace practice. The lower iron content of southern ores gave approximately 2400 lb coke and 2400 lb slag per ton of iron. The richer iron ore of the north gave approximately 1800 lb coke and 1200 lb slag per ton of iron (both practices using about the same average blast temperature). Heat calculations based on Steudel's value of 50 lb extra coke indicate 275,000 Btu of extra input of heat are needed. Nearly half of this heat is consumed in melting the extra slag and burning the extra limestone, part of the remainder being available for processes in the shaft. It must be remembered that, unless the amount of sulphur held by this extra 100 lb slag is substantially greater than that carried in by the 50 lb coke, it is useless to increase slag volume as a means of obtaining low sulphur iron.

Ideally, the silicon content of basic iron should be only 0.7 pct or less, but nearly all low silicon practices show low sulphur ratios of around 15 to 40. These, in general, increase with silicon content, running as high as 100 to 140 at the 1.20 to 1.60 pct Si range. Of course, the increased silicon is in general accompanied by higher coke consumption, partially neutralizing the gain by an increased sulphur burden and lowered production rate.

Increased slag basicity as a very effective means for obtaining higher sulphur ratios also tends to involve a higher coke rate, larger flux requirements, and decreased production. Substitution of MgO for CaO, up to an optimum range of about 6 to 8 pct MgO, is one method which seems to involve no loss in production rate in most cases. If the increased basicity is achieved by the increase of only the CaO, the viscosity of the slag tends to be increased, which



Table III. Comparison of Practices and Sulphur Content of Iron with Increasing Sulphur Content of Coke

| Period of time                             | Furnace D<br>1 Month | Furnace E<br>1 Month | Furnace F<br>1 Month | Furnace G<br>1 Month | Furnace H<br>1 Month | Furnace I<br>1 Week | Furnace I<br>1 Week |
|--------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|---------------------|---------------------|
| Coke sulphur, pct                          | 0.80                 | 0.95                 | 1.30                 | 1.37                 | 1.42                 | 1.66                | 1.83                |
| Coke rate, lb per ton iron                 | 1910                 | 1799                 | 1980                 | 1890                 | 1671                 | 1680                | 1665                |
| Slag, pct SiO <sub>2</sub>                 | 35.1                 | 36.1                 | 34.2                 | 33.1                 | 34.2                 | 33.0                | 33.2                |
| Al <sub>2</sub> O <sub>3</sub>             | 14.3                 | 12.3                 | 12.8                 | 14.3                 | 12.7                 | 13.4                | 13.5                |
| CaO                                        | 44.5                 | 38.3                 | 45.0                 | 42.9                 | 44.6                 | 45.5                | 44.6                |
| MgO                                        | 3.2                  | 8.9                  | 4.4                  | 5.6                  | 5.7                  | 5.0                 | 5.8                 |
| (S)                                        | 1.59                 | 1.30                 | 2.37                 | 2.39                 | 2.49                 | 2.53                | 2.71                |
| Iron, pct Si                               | 0.71                 | 0.83                 | 1.07                 | 0.98                 | 1.10                 | 0.99                | 1.18                |
| Mn                                         | 2.36                 | 0.31                 | 2.85                 | 2.12                 | 2.19                 | 1.87                | 1.83                |
| [S]                                        | 0.036                | 0.042                | 0.029                | 0.037                | 0.042                | 0.030               | 0.033               |
| Pct of casts above 0.050 pct S             | 6.6                  | 18.9                 | 0.8                  | 11.0                 | 22.4                 | 0.0                 | 2.0                 |
| Ratio (S) slag/[S] metal                   | 44                   | 31                   | 82                   | 65                   | 59                   | 83                  | 82                  |
| Slag basicity                              | 1.49                 | 1.50                 | 1.60                 | 1.64                 | 1.64                 | 1.70                | 1.70                |
| Mols (CaO) + Mols (MgO)                    |                      |                      |                      |                      |                      |                     |                     |
| Mols (SiO <sub>2</sub> )                   |                      |                      |                      |                      |                      |                     |                     |
| Slag basicity                              | 1.36                 | 1.31                 | 1.44                 | 1.47                 | 1.47                 | 1.53                | 1.52                |
| Pct (CaO) + Pct (MgO)                      |                      |                      |                      |                      |                      |                     |                     |
| Pct (SiO <sub>2</sub> )                    |                      |                      |                      |                      |                      |                     |                     |
| Slag weight, calculated<br>Lb per ton iron | 1090                 | 1135                 | 1140                 | 1050                 | 1005                 |                     |                     |

in turn requires a higher temperature to maintain a free running slag. However, if the MgO content is raised to about 6 to 8 pct of the final slag composition, the slag then becomes more fluid over a wide range of temperatures, as shown by McCaffery.<sup>2</sup> It was also shown in an earlier paper<sup>3</sup> that MgO in the range of 6 to 8 pct gave a good correlation with lower sulphur in the iron, with one molecule of MgO equal to or better than one molecule of CaO up to this limit.

Any trend toward lower coke consumption by higher blast temperature, or by factors such as sized ores and other charge materials which give greater regularity in operation, will of course favor sulphur removal with no penalty on production rate. Indeed, output rate is usually increased by such methods.

Better contact between metal and slag in the furnace would favor sulphur elimination, but this cannot be controlled by any method now known, except, perhaps, as shown by Steudel,<sup>1</sup> that longer retention of slag favors sulphur absorption, and this is severely limited by the space available below the tuyere level.

In spite of the fact that the theory is yet in dispute, it does appear that in practice a high manganese content in the iron favors increased sulphur ratios as indicated in the paper<sup>3</sup> mentioned above. Even though higher manganese practice does tend to decrease production rate to some small extent, this may be more than offset by the improved sulphur elimination.

As shown in Table III, however, in spite of limitations, the blast furnace can handle a considerable increase in sulphur burden with little or no increase in sulphur content in iron produced. In the cases listed here, the coke-sulphur contents range upward from 0.80 to 1.83 pct, yet all the averages for sulphur in iron remain within the limits of 0.029 to 0.042 pct. Certain points in this group of data may be worth noting, as follows:

Furnaces D and E both used relatively low sulphur coke, 0.80 and 0.95 pct, respectively. Both furnaces produced relatively low silicon iron, 0.71 and 0.83 pct, respectively. Both had approximately the same basicity ratio, 1.49 and 1.50, calculated as mols CaO + mols MgO/mols SiO<sub>2</sub>. However, this relatively low basicity ratio resulted in a moderately low sulphur distribution ratio of 44 for furnace D and 31 for furnace E. An interesting question raised by the comparison is why furnace D had on the average 13

units higher sulphur ratio and hence produced 0.006 pct lower sulphur iron (0.036 as compared to 0.042 for furnace E) despite a 0.12 pct lower silicon iron. The probable reason is the high manganese content of the iron, 2.36 pct, as compared to 0.31 pct for furnace E. It is possible that even greater desulphurization could have been obtained in the case of furnace D if the MgO had been 6 to 8 pct instead of 3.2 pct.

Furnaces F, G, and H had a charge of much higher sulphur coke, 1.30 to 1.42 pct. All three furnaces had comparable silicon contents in iron, 0.98 to 1.10 pct. The three furnaces also had nearly the same basicity, 1.60 to 1.64 mol basis. This basicity ratio is higher than that for the two preceding furnaces discussed above and results in higher sulphur distribution ratios, 59 to 82. Again it is interesting to find that furnace F which had the highest manganese content in the iron (2.85 pct) also had the highest sulphur ratio (82) and hence the lowest sulphur content of iron (0.029 pct) as compared with 0.037 and 0.042 pct for the other two furnaces.

Finally, the two separate weekly tabulations of furnace I represent a charge of still higher coke sulphur, 1.66 and 1.83 pct. Despite these high values the iron averaged relatively low in sulphur content (0.030 and 0.033 pct) with fairly high sulphur ratios (83 and 82). These values resulted mainly from the very high basicity, 1.7 mol basis. This is the highest basicity ratio of all the data listed in Table III. Also contributing to this high degree of desulphurization was the medium silicon (0.99 and 1.18 pct) and manganese (1.87 and 1.83 pct) contents together with a medium magnesia content of 5.0 and 5.8 pct. Probably even greater desulphurization would have resulted if the manganese in the iron had been higher.

In the paper by Kennedy and Thornton<sup>4</sup> a series of slag compositions were studied with respect to sulphur removal. In going from 0 to 100 pct dolomite flux charge it was found that the 35 pct dolomite, 65 limestone charge produced the maximum desulphurization. In Table I of their paper is shown the average results of 70 bessemer iron casts of this charge. Briefly the results can be summarized as follows:

The average sulphur distribution ratio was 101, which resulted in 0.018 pct sulphur in the iron. This high degree of desulphurization was achieved: 1—by a high basicity ratio (1.66 mol basis or 1.50 percentage basis) accompanied with 6.1 pct MgO in the

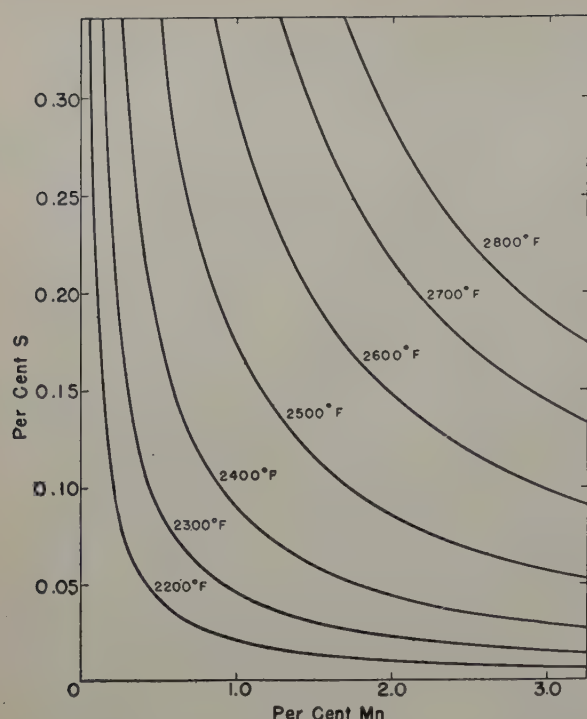


Fig. 1—Solubility of manganese and sulphur in hot metal as a function of temperature.

slag, and 2—with a high silicon content of the iron (1.53 pct) which indicates a high hearth temperature (2750°F average flush slag temperature). It is interesting to note that the manganese in the iron was only 0.50 pct, which illustrates how high slag basicity, temperature, and silicon content can over-balance the countereffect of a low manganese level.

In Fig. 9 of this same paper<sup>4</sup> is shown the distribution curve of the sulphur distribution ratio for the individual casts which varies from 70 to 160. These upper values of 150 and 160 represent about the maximum values that we have obtained on individual casts. The usual range of observed values of this ratio vary from 20 to 125 based on composites of 12 and 24 hr samples (2 to 4 casts).

### External Desulphurization of Iron

It has been suggested that the problem of sulphur in iron can best be solved by operating the blast furnace without reference to the sulphur, which is then brought down to a satisfactory level by some special treatment of the liquid iron after it has been removed from the furnace.

External desulphurization has been accomplished mainly with alkalis. This method has been employed in many foundries for some time as well as a number of blast furnace plants for the treatment of off-casts high in sulphur. As a result, a number of papers have been written on this subject.

Various methods for external desulphurization may be listed and discussed briefly as follows:

The use of alkalis or mixtures as follows: soda ash ( $\text{Na}_2\text{CO}_3$ ) with 58 pct  $\text{Na}_2\text{O}$ ; caustic soda ( $\text{NaOH}$ ) with 76 pct  $\text{Na}_2\text{O}$ ; soda ash and caustic soda mixtures; and soda ash, limestone, and fluorspar mixtures. The alkalis are produced in granular or briquette form. The advantage of the latter is that boiling action is prolonged by slower melting of the lumps. These alkalis are commonly added to the bottom of the ladle before casting or to the iron stream flowing into the ladle. Sometimes a combina-

tion of both methods is used. Obviously contact between alkali and metal is obtained by the stirring action of the falling iron stream and the boiling action of the desulphurizing material. Such a means of making contact is bound to be erratic from one addition to another. Hence a variable amount of sulphur reduction results from cast to cast. It has also been found that a high sulphur content in the iron can be lowered quite consistently to the 0.040 to 0.050 pct range, but considerable difficulty is encountered in attempting to bring it down near 0.030 pct or below. Further complications arise from the reaction of this alkaline slag with the silica refractory of ladles and mixer. This in turn results in increased refractory costs. Finally, if proper separation of this desulphurizing slag and kish is not made at the ladles or mixer, it will be charged into the open hearth furnaces. How much of this extra sulphur is oxidized and removed in the gas phase, or passes out with flush slag in heats using a runoff practice, is quite debatable. An elaborate layout of ladles equipped with facilities for the separation of the spent desulphurizing slag is discussed by Evans.<sup>5</sup> This method eliminates some of the variation in sulphur reduction but it will not aid in the desulphurization to a low sulphur level.

The desulphurization of iron has also been accomplished with calcium carbide. Laboratory experiments on the method of adding this material were made by Wood<sup>6</sup> and coworkers. It is interesting to note that by rapid stirring in of fine calcium carbide below the iron surface a sulphur elimination ranging from 63 to 93 pct was obtained. This illustrates the intimate contact that must be made between surfaces of liquid metal and the desulphurizing media.

It has been reported by Warren<sup>7</sup> that the sulphur content of iron decreased somewhat during an abnormally long interval between casting into transfer ladles and delivery to the mixer in the open hearth shop. A detailed study of metal and kish samples from Warren's practice, which also included X-ray diffraction patterns, indicated the presence of  $\text{MnS}$ . These data tend to confirm the reality of  $\text{MnS}$  separation from iron. However, this should occur only when manganese and sulphur contents are high enough, and the final temperature low enough, to cause supersaturation. For illustration, Fig. 1 presents a family of solubility curves of manganese and sulphur in liquid iron for various temperatures based on Joseph and Holbrook's findings.<sup>8</sup> If the analyses of the above mentioned samples are compared to this chart the effects indicated are as follows:

When cast into the ladle at the blast furnace the iron contained 0.085 pct S and 1.90 pct Mn. The iron cooled during the 3 to 4 hr travel to the mixer and when it reached a temperature of approximately 2490°F solid  $\text{MnS}$  began to separate. This continued until the final composition at the mixer was 0.042 pct S and 1.82 pct Mn. On this diagram this corresponds to approximately 2380°F. On the basis of the solubility diagram, it would usually be possible to reduce the sulphur on high sulphur casts by cooling the ladles of metal to approximately 2400°F. The final sulphur content, at this temperature, would obviously depend on the manganese content of the iron. For example, if the manganese content were below 1.0 pct the final sulphur content would not be reduced below 0.090 pct. However, if the manganese content were 1.75 pct, the final sulphur would then be down to 0.05 pct; and if the manganese content



were further increased to 2.8 pct, the sulphur would be reduced to 0.03 pct.

Prerequisites for this method of sulphur reduction are high manganese iron, longer delivery time to the mixer, and lower temperature iron entering the mixer. The two latter requirements are the most objectionable from the standpoint of speed of operation. Besides these three requirements a good separation of the solid MnS and kish should be made before the iron enters the mixer.

In general, it appears evident at this time that future developments in desulphurization between blast furnace and open hearth should trend toward improved and better controlled contact between metal and desulphurizing agent; minimum costs of material and labor; and less cooling of the metal. Increased dependence on lime, as the cheapest and most effective sulphur absorber, seems probable. If the desulphurizing unit could be incorporated in, or take the place of, the regular iron mixer, this would be best adapted to the flowsheet of the normal steel plant.

### Sulphur Problem of the Open Hearth

The reduction of sulphur in the open hearth bath is more difficult and is limited to much smaller amounts than the reduction in the blast furnace. This is exemplified by: 1—the difference in sulphur distribution ratios, with observed values of from about 2 to 12 in the open hearth, whereas in the blast furnace the range is from 15 to 150; 2—the inherent nature of the open hearth, with its pattern of heat flow largely from above through the slag layer, limits the practical slag weight to from 8 to 18 pct of the metal weight as compared to a range of 40 to 150 pct in various blast furnace practices.

Consequently the sulphur burden or total sulphur input into the individual open hearth heats becomes of primary importance. Before discussing various specific sulphur balances and burdens, it might be well to consider briefly the different items that make up the input side of the sulphur balances. These items are listed as follows:

**Liquid Iron or Hot Metal:** The amount of sulphur introduced into the open hearth charge in the liquid iron usually accounts for 27 to 50 pct of the total sulphur input. This of course depends mainly on the amount of liquid iron addition which usually corresponds to from 40 to 70 pct of the total weight of scrap and hot metal. Open hearth shops making much of their product to rather low sulphur specification may desire the percentage of sulphur in the hot metal to average below 0.030 pct. Shops producing steel with a less critical sulphur specification frequently average 0.040 pct S or higher in the liquid iron.

There is another source of sulphur which is introduced with the hot metal and is commonly called kish. This material is heterogeneous and erratic in both physical and chemical makeup. It consists of oxidized metal shot, coke fines (thrown on the top of the iron ladles), fire clay, silica (from ganister refractories and sand of the runner and cast house floor), separating particles of MnS, and frequently blast furnace slag. The primary components of the kish which contribute sulphur are the coke fines, the slag, and the MnS phase, and they represent a wide range of sulphur contents (see Table IV). The rather high silica content (10 to 35 pct) of kish has a deleterious effect on the sulphur removal from the open hearth bath because it counteracts the basicity of the slag. These detrimental effects of kish are obvi-

Table IV. Typical Ranges of Sulphur in Some Charge Materials

| Materials              | S. Pct    |
|------------------------|-----------|
| Limestone              | 0.03-0.20 |
| Burnt lime             | 0.02-0.25 |
| Raw dolomite           | 0.02-0.40 |
| Single burned dolomite | 0.02-0.25 |
| Double burned dolomite | 0.01-0.20 |
| Fluorspar              | 0.10-2.00 |
| Kish                   | 0.30-0.80 |

ously most serious in the case of open hearth heats without runoff slags. The kish probably tends to float on the slag in the open hearth as the iron is charged. Some rather recent samplings of runoff slags have indicated that the first portions of the runoff are often higher in sulphur than would be expected from slag-metal equilibria. These data suggest that much of the kish entering the open hearth is floated or carried out by the runoff slag, at least in those heats having the start of flush immediately or shortly after the time of the hot metal addition.

**Scrap:** The amount of sulphur introduced into the open hearth charge from scrap is somewhat variable, obviously depending on its sulphur content and the amount charged (governed largely by the hot metal percentage of the particular shop). The sulphur content of the scrap that is produced in a given shop should be known reasonably well, especially if steps are taken to separate the high sulphur steel scrap from the ordinary scrap lower in sulphur. However, the sulphur content of purchased scrap is practically unknown; this is especially true of the miscellaneous scrap. This introduces considerable uncertainty in the sulphur burden if large quantities of purchased scrap are charged.

Recent findings of Osborne<sup>9</sup> indicate that the rust attached to the scrap may have a sulphur content 15 to 18 times greater than the base metal. From Table I of his paper, the average sulphur content of the base metal was 0.0206 pct and that of the rust accompanying this scrap was 0.324 pct. In this connection, we have collected different rust samples from various scrap piles of our plants. These rust samples had been formed over a period of one to seven years and gave sulphur contents varying from 0.20 to 1.10 pct with an average of 0.50 pct. It is interesting to note that if we assume that the scrap averaged 95 pct metal with 0.030 pct S and 5 pct rust with 0.50 pct S, the aggregate sulphur content of the scrap would then be 0.054 pct. This would result in a very appreciable increase in sulphur burden if an appreciable amount of rust were charged on some heats. However, it is difficult to know what percentage rust is present in most scrap and there is also the possibility that the sulphur in the rust would be vaporized out during melting, although Fig. 2 of Osborne's<sup>9</sup> paper does not tend to substantiate this idea.

From this discussion it can be seen how difficult it is to obtain a representative sulphur content for the scrap to be used in calculating a sulphur input balance. To obtain such a value good clean scrap free of rust and of known composition must be used.

**Limestone, Burnt Lime, and other Fluxes:** The chemical analyses of numerous shipments of the various fluxes (see Table IV) have revealed a wide variation in sulphur content. This variation usually represents differences between quarries, although considerable variation sometimes exists in shipments



Table V. Comparison of the Ladle Sulphur Content of Heats Charged with High and Low Sulphur Limestone Content

| Time              | No. of Heats | Avg. S Content of Limestone | Avg. Pct Ladle S |
|-------------------|--------------|-----------------------------|------------------|
| First six months  | 616          | 0.160                       | 0.0285           |
| Second six months | 872          | 0.045                       | 0.0245           |
| Difference        |              | 0.115                       | 0.0040           |

from the same quarry. Table IV gives typical ranges from a large number of individual determinations.

The users of fluxes high in sulphur content are very likely to pay a penalty in the form of higher final sulphur contents. This is illustrated by the following example which is a comparison of heats for similar low carbon grades made over two consecutive six-month periods. The open hearth fuel was natural gas (hence there was no sulphur pickup from the furnace gases). The steel was made on a runoff practice with comparable limestone charge, scrap, and iron analysis. The main difference was the sulphur content of the limestone as shown in Table V.

This is quite understandable when it is realized that the ratio of weight of steel to the weight of tap slag varies from about 7:12, whereas the slag to metal sulphur ratio at tap is most commonly about 4:7. Even on heats with maximum sulphur specifications of 0.04 to 0.05 pct, limestone with more than around 0.25 pct S may add more sulphur to the burden than it can remove; in heats for steel with maximum sulphur of 0.020 pct or below, this critical value may be down toward 0.10 pct S or lower. For the same reason the sulphur content of burnt lime and dolomite should be kept as low as possible.

It is worth remembering that the moderate amount of sulphur removed in runoff slag may come from charge ore, scrap, hot metal, or dolomite on banks, but all the sulphur in the charged limestone contributes to the sulphur carried in the final slag and metal at tap. Higher sulphur in dolomites used may contribute sulphur to both runoff and tap slags.

*Ore, Sinter, and Miscellaneous Additions:* The sulphur content of ore, sinter, and alloy additions should be kept as low as possible. It is realized that often only one type of ore, sinter, or other material is available at the particular plant and must be used. However, when a choice can be made between similar materials that are reasonably comparable in other respects except sulphur contents, then the one which has the lowest sulphur content should be used.

*Fuel:* The total amount of sulphur charged from all the sources just discussed above, from hot metal to ore, usually varies from a low of 0.65 lb to a high of 1.25 lb S per ton of steel.

In considering open hearth fuels it is found that the total amount of sulphur available from this source varies widely with the different types of fuels. Also that all the fuels except natural gas have an amount of sulphur that exceeds the total from all other input sources. This is illustrated in Table VI which represents typical values for present day fuels.

It is very fortunate that this relatively high sulphur potential of the fuel is transferred to the slag-metal system at a very low efficiency. With fuels having lower sulphur contents (similar to fuels used 12 to 17 years ago), it is doubtful whether any appreciable amount of sulphur enters the metal.

This point will be discussed in more detail a little later. The studies of Diehl<sup>10</sup> and others of the sulphur equilibrium between metal and sulphur-containing gases show that an increase in oxygen pressure decreases the tendency toward sulphur absorption from the gas. During the melting of scrap in the open hearth the scrap is piled fairly high in the furnace and is bathed by portions of the flame containing incompletely combusted fuels to give a low oxygen pressure, favoring sulphur pickup from the fuel.

Conversely the factors which minimize the sulphur pickup from a high sulphur fuel during scrap melting may be enumerated as follows: 1—rapid scrap charging, 2—maintenance of a high ratio of air to fuel with a short oxidizing flame, 3—rapid melt down, and 4—avoidance, as much as possible, of a high pile of scrap that remains for a considerable period of time in the direct path of the flame.

It has frequently been found, when calculating sulphur balances, that the input side was less than the output. This difference has often been captioned "unaccounted for (from furnace gases)." It is thus assumed that the unaccounted for sulphur represents the sulphur absorbed from the fuel during the scrap melting. Actually, however, the amount of unaccounted for sulphur which can be attributed to the fuel is rather difficult to estimate. For example, under our discussion of the sulphur content of scrap it was pointed out that 5 pct rust on the scrap would increase the aggregate sulphur content approximately 80 pct. Sulphur contents in such rust, in kish spilled in with hot metal, and in eroded dolomite are frequently overlooked. The point is that an error in the sulphur content of some of the charged materials could easily account for all or nearly all the missing sulphur of the balance in most cases. The fact that, when the sulphur content of the fuel is relatively low, or only moderately high, the amount of sulphur absorbed during scrap melting is rather small tends to be substantiated by data obtained approximately 15 years ago when the sulphur content of fuels was lower than that in present fuels.

These data from several plant practices are tabulated in Table VII and, for each plant, represent an average of ten heats of the same grade of steel. All 50 heats were carefully made with complete details of weights and analyses of incoming materials and outgoing products. It is believed they represent a very good set of data for calculating balances. Table VII is confined to the sulphur balance data.

As nearly as could be ascertained, all the heats were charged with fairly clean scrap and the amount of rust introduced with the scrap was rather insignificant, consequently the sulphur content of the base scrap metal was probably close to the true value. Hence it would seem that the amounts of sulphur charged into these heats are truly representative. Thus for these particular heats the unaccounted

Table VI. Average Amount of Sulphur Available in the Various Fuels

| Materials                 | Lb S per Ton Steel | Equivalent Pct S in Steel |
|---------------------------|--------------------|---------------------------|
| All other input materials | 0.65 to 1.25       | 0.033-0.063               |
| Natural gas               | 0                  | 0                         |
| Tar and natural gas       | 1.25               | 0.063                     |
| Oil                       | 2.15               | 0.108                     |
| Tar                       | 2.50               | 0.125                     |
| Tar and coke oven gas     | 4.25               | 0.213                     |
| Coke oven gas             | 6.00               | 0.300                     |



for sulphur probably represents a fairly good estimate of the sulphur pickup from, or loss to, a group of fuels with low to moderate content of sulphur.

In discussing the results of Table VII, consider first the data from plants A and B:

In the case of plant A, the fuel was a mixture of 62 pct natural and 38 pct coke oven gas with a relatively low total sulphur content of 0.79 lb per ton (from the coke oven gas). The unaccounted for sulphur amounted to only 0.01 lb per ton or 1.5 pct of the total sulphur charged and is on the output side of the balance, indicating a loss of sulphur from the slag-metal system to the gas phase.

In the case of plant B, a mixed fuel was used which consisted of 58 pct natural gas and 42 pct tar. Again this fuel had a relatively low total sulphur content of 0.70 lb per ton (from the tar). The unaccounted for sulphur of the balance amounted to 0.11 lb per ton or 12.9 pct of the total sulphur, once more on the output side of the balance. The unaccounted for sulphur of the balance (0.11 lb per ton) seems rather high and could be due, in part, to some other errors of the sulphur contents of input or output materials. In any case, the data of this plant indicate a net loss of sulphur to the gas phase.

In discussing the remaining data of Table VII the result of plants C, D and E will be considered together as follows:

Two plants (C and D) used producer gas whereas the third plant (E) used 80 pct tar and 20 pct coke oven gas. The sulphur content of these fuels varied from 1.80 to 2.17 lb S per ton steel, or more than double the sulphur content of fuels of plants A and B. The unaccounted for sulphur, of the balance, varied from 0.01 to 0.03 lb S per ton steel or 1.5 to 4.4 pct of the total sulphur of the balance. In all three cases the unaccounted for sulphur is on the input side of the balance indicating a pickup of sulphur from the fuel. If we consider the fuel as contributing all the unaccounted for sulphur, it will be noted that this is fairly small and amounts to only 1.5 to 4.4 pct of the total sulphur burden. If this unaccounted for sulphur is compared with the sulphur content of the fuel, the low efficiency of the sulphur transfer is apparent:

Plant C

$$\frac{0.03 \text{ lb S per ton unaccounted for}}{1.84 \text{ lb S per ton in fuel}} \times 100 = 1.6 \text{ pct}$$

Plant D

$$\frac{0.03 \text{ lb S per ton unaccounted for}}{2.17 \text{ lb S per ton in fuel}} \times 100 = 1.4 \text{ pct}$$

In other words it appears that a maximum of 1.0 to 2.0 pct of the sulphur of the fuel is absorbed by the slag-metal system during melting at these intermediate levels of fuel sulphur content.

In some of the present day higher sulphur fuels (4.0 to 6.0 lb S per ton steel) which some of the plants are forced to use from time to time, a larger transfer and absorption of sulphur from the fuel is noted. To illustrate this point the experience of several plants may be noted briefly as follows:

One plant normally had a supply of open hearth fuel oil that averaged 1.0 pct S. With this fuel the desired ladle sulphurs were obtained with an average slag basicity of approximately 2.6. For a period of one to two months this plant had to use a fuel oil containing over 3.0 pct S. It was soon found that

Table VII. Comparison of the Sulphur Content of the Fuel with the Unaccounted for Sulphur of the Sulphur Balance

| Item                      | Plant A                                |       | Plant B                          |       | Plant C      |       | Plant D      |       | Plant E                        |       |
|---------------------------|----------------------------------------|-------|----------------------------------|-------|--------------|-------|--------------|-------|--------------------------------|-------|
|                           | Lb                                     | Pct   | Lb                               | Pct   | Lb           | Pct   | Lb           | Pct   | Lb                             | Pct   |
| S in all charged material | 0.66                                   | 100.0 | 0.81                             | 100.0 | 0.73         | 95.6  | 0.87         | 96.1  | 0.64                           | 98.5  |
| Unaccounted for           |                                        |       |                                  |       | 0.03         | 4.4   | 0.03         | 3.9   | 0.01                           | 1.5   |
| Total input               | 0.66                                   | 100.0 | 0.81                             | 100.0 | 0.76         | 100.0 | 0.90         | 100.0 | 0.65                           | 100.0 |
| S in liquid steel         | 0.46                                   | 69.7  | 0.45                             | 56.3  | 0.50         | 66.2  | 0.47         | 52.1  | 0.46                           | 70.7  |
| S in runoff slag          | 0.09                                   | 13.7  |                                  |       |              |       |              |       |                                |       |
| S in final slag           | 0.10                                   | 15.1  | 0.25                             | 30.8  | 0.26         | 33.8  | 0.43         | 47.9  | 0.19                           | 29.3  |
| Unaccounted for           | 0.01                                   | 1.5   | 0.11                             | 12.9  |              |       |              |       |                                |       |
| Total output              | 0.66                                   | 100.0 | 0.81                             | 100.0 | 0.76         | 100.0 | 0.90         | 100.0 | 0.65                           | 100.0 |
| Type fuel                 | 62 pct natural gas<br>38 pct coke oven |       | 58 pct natural gas<br>42 pct tar |       | Producer gas |       | Producer gas |       | 80 pct tar<br>20 pct coke oven |       |
| S in fuel, lb per ton     | 0.79                                   |       | 0.70                             |       | 1.84         |       | 2.17         |       | 1.80                           |       |

in order to finish the heats with the same ladle sulphur as before, the slag basicity had to be increased to 3.5 to 3.8. After the plant again returned to its regular oil supply containing 1.0 pct S the lime and limestone consumption decreased to its regular value. Several sulphur balances were made on another plant using coke oven gas with high sulphur contents (4.0 to 5.0 lb S per ton steel). These particular sulphur balances are fairly accurate but probably not as good as those shown in Table VII. Consequently, we cannot be sure that all the unaccounted for sulphur came from the fuel, though it is quite possible that a large fraction was contributed by the fuel. This will be discussed further a little later in connection with some other data. Returning to the sulphur balances, the unaccounted for sulphur varied from 0.17 to 0.34 lb S per ton steel. Comparing these values with the sulphur content of the fuel the following variation is noted:

For one balance:

$$\frac{0.17 \text{ lb S per ton unaccounted for}}{4.0 \text{ lb S per ton in fuel}} \times 100 = 4.3 \text{ pct}$$

For another balance:

$$\frac{0.34 \text{ lb S per ton unaccounted for}}{4.8 \text{ lb S per ton in fuel}} \times 100 = 7.1 \text{ pct}$$

Thus it appears from these data that a maximum of 4.0 to 7.0 pct of the sulphur in the fuel was transferred to, or absorbed by, the slag-metal system during melting, at these high levels of sulphur content of the fuel. This gain of sulphur from the fuel is of sufficient magnitude to raise the ladle sulphur content by approximately 0.006 to 0.010 pct S. Other experiments with high sulphur coke oven gas have shown that a substantial reduction in final ladle sulphur contents can be obtained if desulphurized coke oven gas is used during the scrap melting period of the heat. One or more erratic conditions probably exist in normal practice, causing variability in sulphur absorption from gases; further study is needed here.

The sulphur problem of the open hearth, as discussed so far in this paper, has been centered on the input of the sulphur balance including the various types of fuel. The remainder of this discussion will

Table VIII. Average Sulphur Balance for Groups of 10 Heats.  
No Runoff Practice

| Item                                     | Plant D                     |                 | Plant E                     |                 |
|------------------------------------------|-----------------------------|-----------------|-----------------------------|-----------------|
|                                          | Lb<br>S per<br>Ton<br>Steel | Pct of<br>Total | Lb<br>S per<br>Ton<br>Steel | Pct of<br>Total |
| S charged in scrap                       | 0.35                        | 39.0            | 0.30                        | 46.1            |
| S charged in liquid iron                 | 0.26                        | 28.3            | 0.25                        | 38.5            |
| S charged in limestone                   | 0.14                        | 15.6            | 0.09                        | 13.9            |
| S charged in fluorspar                   | 0.12                        | 13.2            |                             |                 |
| Unaccounted for                          | 0.03                        | 3.9             | 0.01                        | 1.5             |
| Total input                              | 0.90                        | 100.0           | 0.65                        | 100.0           |
| S in liquid steel                        | 0.47                        | 52.1            | 0.46                        | 70.7            |
| S in final slag                          | 0.43                        | 47.9            | 0.19                        | 29.3            |
| Total output                             | 0.90                        | 100.0           | 0.65                        | 100.0           |
| Limestone and equivalents,<br>lb per ton | 172                         |                 | 152                         |                 |
| Weight of final slag,<br>lb per ton      | 192                         |                 | 167                         |                 |
| Basicity ratio                           | 3.94                        |                 | 2.32                        |                 |
| Pct S in metal                           | 0.024                       |                 | 0.023                       |                 |
| Pct S in Slag                            |                             |                 |                             |                 |
| Ratio                                    | 9.3                         |                 | 5.1                         |                 |
| Pct S in Metal                           |                             |                 |                             |                 |
| Pct S in slag                            | 0.223                       |                 | 0.117                       |                 |

deal with the output side of the sulphur balance and with the metallurgical problems that arise when it is desired to lower the sulphur content of the bath during the refining period. The situation can best be outlined by tabulating a couple of sulphur balances and referring to certain points of interest. For this purpose the complete sulphur balances of plants D and E of Table VII are repeated more in detail in Table VIII.

It will be noted that a difference exists between the total input sulphur of the two plants. Plant D has a heavier sulphur burden input, largely due to the higher sulphur content of the fluorspar and limestone. The larger sulphur input of plant D required a larger slag volume and heavier limestone charge to give the higher sulphur ratio of 9.3 as compared to 5.1 for plant E. The most interesting point in the practice at plant D is that the high slag basicity of 3.94 produced a sulphur content of only 0.024 pct, whereas plant E obtained 0.023 pct S in the metal with a slag basicity of only 2.32. Obviously such a practice as that used by plant D is uneconomical both in cost of material and increased time of heat. At a later period, plant D obtained new sources of these materials with lower sulphur contents and was able to decrease slag volume and basicity without changing the sulphur content of the final steel.

It is generally agreed by most investigators that the open hearth process is a poor desulphurizer, so that a small amount of excess sulphur requires a relatively large excess of basic materials (CaO and MnO) and large slag volumes. It is further agreed that the observed sulphur ratio (of sulphur in slag to sulphur in metal) is increased by free CaO (that CaO remaining after the SiO<sub>2</sub> and the P<sub>2</sub>O<sub>5</sub> have been chemically satisfied) and free MnO in the open hearth slag.

There is some disagreement among various investigators on the method of calculating the sulphur ratio between slag and metal from the ordinary open hearth slag analysis. One method of calculation has been proposed by Darken and Larsen<sup>11</sup> and another by Grant and Chipman.<sup>12</sup> Somewhat different results from the two methods illustrate the difficulties that arise with a multicomponent system such as an open hearth slag.

The sulphur balances of Table VIII were for heats of a no-runoff practice, with a relatively low percentage of liquid iron in the charge, in the range of 35 to 45 pct. In recent years it has been the practice for a number of plants to operate with much higher liquid iron percentages in the range of 50 to 70 pct. Such a practice necessitates running or flushing off the early premelt slag prior to the lime boil. Obviously such a practice has both advantages and disadvantages. However, these will be discussed only with respect to the sulphur problem.

The advantages are that if the runoff practice is properly executed to give a maximum runoff slag, approximately 55 to 65 pct of the total silica and 14 to 20 pct of the total sulphur is eliminated.

The disadvantages are as follows: In a good runoff slag practice approximately 55 to 65 pct of the total Mn is eliminated as MnO. As a result, the refining slag is lower in MnO which in turn produces a lower sulphur ratio between slag and metal. A further disadvantage occurs when a poor slag runoff is obtained. In such cases only about 30 to 50 pct of the total silica and 8.0 to 13.0 pct of the total sulphur is removed from the system. The extra silica, and also the sulphur that is not flushed off, are added to the refining slag. This additional silica requires practically all the extra charged limestone to neutralize it. Consequently the slag after melting is not very basic and requires variable, and frequently large, additions of extra burned lime to produce the desired desulphurization of the bath. Such a condition causes poor control of slag shaping and lowered production rate.

The importance of maintaining a good runoff of slag from heat to heat cannot be overemphasized. This requires constant supervision from the foreman and furnace operator.

### Sulphur Problems After Tap

Ordinarily there is no appreciable change in sulphur content of steel as it is tapped from the furnace and teemed into the ingot mold. Occasionally heats are encountered in which the final steel sulphur has increased 0.002 to 0.004 pct. It will be found that in such cases the tap slag is of low basicity ratio, nearly on the acid side. In addition such heats are usually blocked and silicon killed. Consequently the furnace slag, already low in basicity as it enters the ladle, becomes more acid because of the extra silica from the ferro-silicon ladle addition and because of the ladle refractory erosion, the resultant effect being to cause a reversion of both sulphur and phosphorus to the metal.

In contrast we have found that silicon-killed steel to which calcium-silicon ladle additions have been made show a decrease in final sulphur. We have carefully checked nearly a dozen heats to which 3.5 to 5.0 lb CaSi per ton of steel was added and find that sulphur content of the steel has decreased 0.002 to 0.004 pct from the tapping to the teeming operation.

### Summary

In the steelmaking cycle the largest source of sulphur is in the coal used to make coke for the blast furnace. Efforts to remove any appreciable amount of sulphur from the coal or the coke have so far been impracticable because of the low activity of the organic sulphur in the coal and coke and because of the price limitations involved in treating a low cost material such as coke.



Sulphur balances of the blast furnace indicate that 88 to 94 pct of the sulphur input is from the coke and 94 to 96 pct of the total sulphur is carried out in the blast furnace slag.

Cokes with average sulphur content in the range 0.80 to 1.80 pct have been charged in the blast furnace and iron with sulphur content of 0.036 to 0.042 pct has been produced. This was possible with an increase in slag basicity, addition of dolomite to produce a slag with 5 to 8 pct MgO, and by increasing the manganese content of the iron with increased open hearth slag additions.

External desulphurization of the iron has been accomplished by the use of alkalies and calcium carbide. Also iron with high manganese content can be desulphurized by holding the ladles for an extra 2 to 4 hr and thereby lowering the iron temperature to allow the separation of MnS.

The reduction of sulphur in the open hearth is more difficult than in the blast furnace. This is illustrated by the sulphur distribution ratios which are 10 to 12 times lower in the former process. For this reason the sulphur content of each raw material charged should be kept to the absolute minimum. This is especially true of limestone, burnt lime, the various dolomites, fluorspar, kish, and also rusty scrap. Evidence is presented to show that the charging of fluxes high in sulphur results in several points increase in the final ladle sulphur analysis.

The total amount of sulphur available from the open hearth fuels varies widely with the different types of fuels. All the fuels except natural gas carry in an amount of sulphur that exceeds the total from all other input sources. Although the percentage of this sulphur which is transferred to the slag metal system is generally rather poor, it tends to increase at the higher fuel sulphur levels, so that those fuels highest in sulphur content do contribute an appreciable amount. The amount of this sulphur absorption is variable with furnace operating conditions during scrap charging and melting.

Complete sulphur balances of open hearth heats are shown; these indicate the importance of minimum weight of  $\text{SiO}_2 + \text{P}_2\text{O}_5$  in the tap slag, also the need to both increase basicity and increase manganese oxide of the slag to further lower the sulphur content of the bath during the refining period.

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## Technical Note

## Useful Etchants for Electron Metallography

by William L. Grube

**S**PECIMEN preparation for electron metallography involves several steps, such as polishing, etching, replicating, mounting, and shadowing. Although each step must be done with care, the operation requiring the utmost attention is etching.

Proper etching is important because the relief pattern developed on the surface of the specimen by the etchant, and reproduced as minute differences in thickness of the replica, determines entirely the amount of detail seen in the final micrograph. The characteristic colored stains, sometimes used in light metallography to simplify identification of certain microconstituents, cannot be tolerated because there

is danger of introducing artifacts in the replicating operation. It is also quite difficult to remove plastic replicas from stained specimens. A suitable etchant for electron metallography must, therefore, in all cases exhibit a preferential attack upon each of the microconstituents present sufficient to result in a difference in surface elevation.

When only two microconstituents are present, it is not too difficult to find a suitable etchant since their physical or chemical properties are generally sufficiently different to result in a marked difference in attack by the etchant. For example, picral (a saturated solution of picric acid in methanol used as an immersion etch) is a satisfactory etchant for the specimen shown in Fig. 1 consisting of iron carbide particles embedded in a ferrite matrix.<sup>1</sup>

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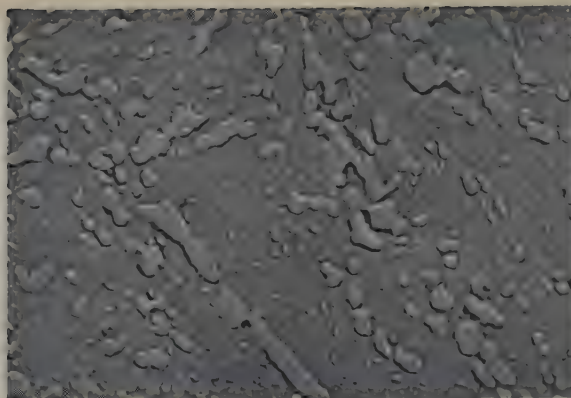


Fig. 1—Tempered martensite. 1100°F, 1 hr. Etched in 4 pct picral. X5000.

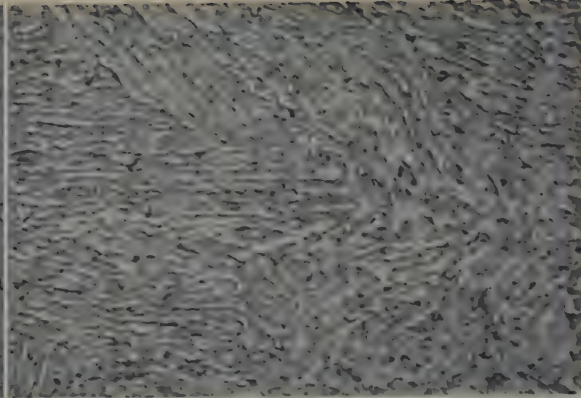


Fig. 2—Fine pearlite. I.T. 1100°F. Etched in 4 pct picral. X5000.

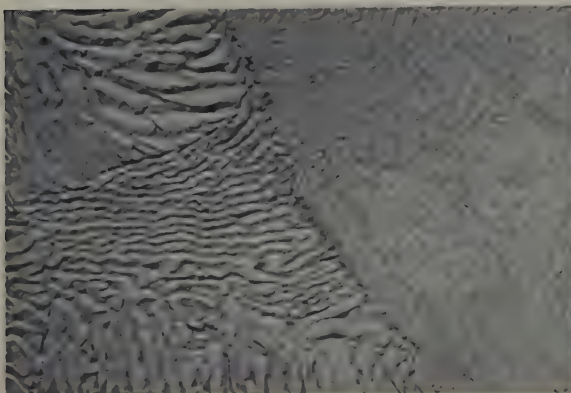


Fig. 3—Fine pearlite. I.T. 1100°F. Etched in  $\text{FeCl}_3 \cdot \text{HCl}$ . X5000.

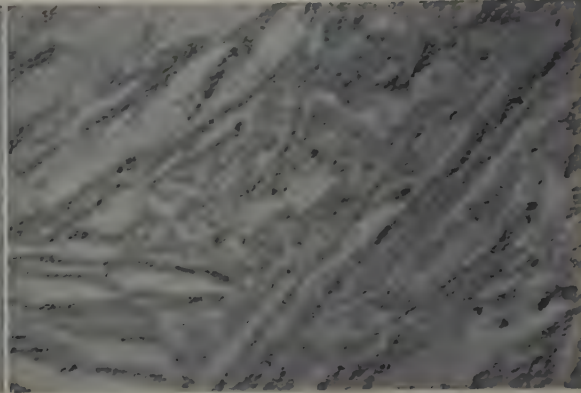


Fig. 4—Martensite as-quenched. Etched in 4 pct picral. X5000.

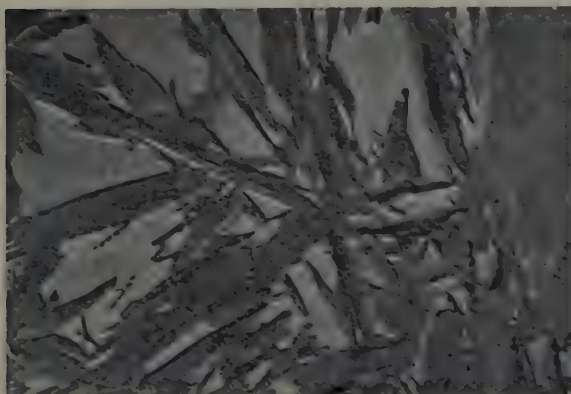


Fig. 5—Martensite as-quenched. Etched in 2 pct nital plus zephiran chloride. X5000.

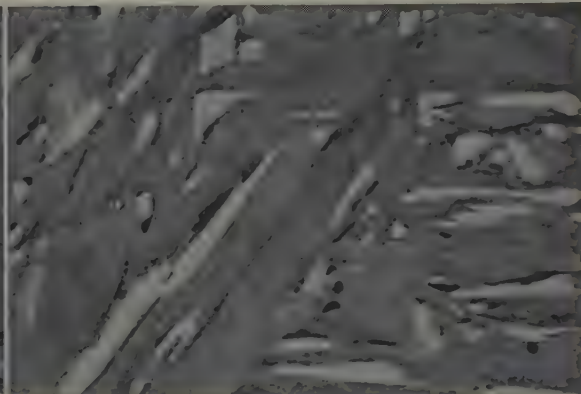


Fig. 6—Martensite as-quenched. Etched in Allten's reagent. X5000.

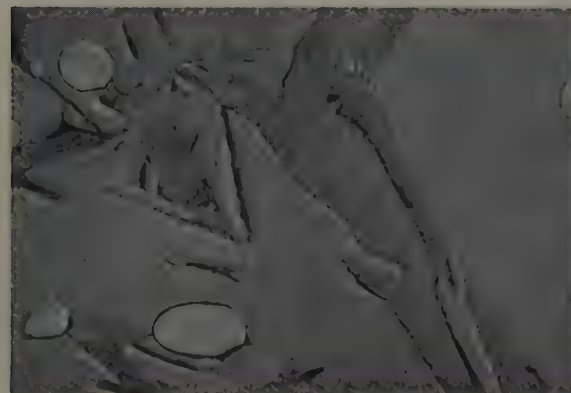


Fig. 7—S.A.E. 52100 steel. Etched in 2 pct nital. X5000.

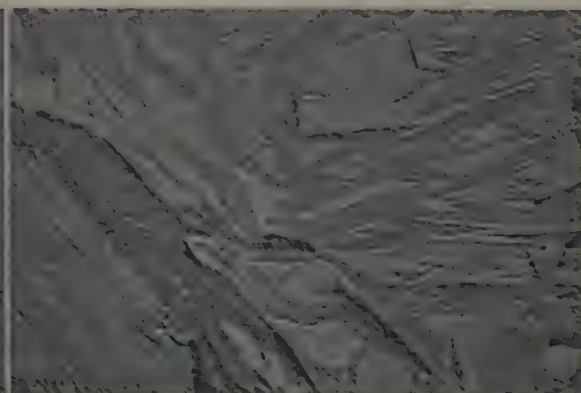


Fig. 8—S.A.E. 52100 steel. Etched in 2 pct nital plus zephiran chloride. X5000.





Fig. 9—Cemented tungsten and tantalum carbides. Composite electrolytic alkaliferri cyanide and 3 pct nital etch. X5000.



Fig. 10—Carbide in Vitallium. Vacuum-cathodic etch. X5000.

Picral is less satisfactory when used to etch fine lamellar pearlite shown in Fig. 2. Although the relief is sufficiently developed, the etchant has left a residue upon the surface as indicated by the presence of small opaque particles. Moreover, some irregularities appearing in the carbide lamellae indicate that the replica adhered to the specimen tightly and suffered some disturbance upon removal.

A more satisfactory etchant for fine pearlite is ferric chloride-hydrochloric acid (1 pct HCl; 2 pct  $\text{FeCl}_3$  in methanol). As shown in Fig. 3, this etchant leaves a cleaner surface for replicating. Also differences in orientation of the pearlite colonies are more clearly resolved.<sup>1</sup>

As pointed out earlier by Ellis<sup>2</sup> it is quite difficult to etch the harder microstructures of steel (those containing martensite as-quenched, slightly tempered, or both) satisfactorily for electron metallography. For as-quenched steels, the etchant must, essentially, differentiate between martensite and retained austenite. This picral will not do, as indicated in Fig. 4. A modified nital etchant<sup>3</sup> consisting of 2 pct nital containing 0.5 to 1.0 pct zephiran chloride is almost ideal for this structure as shown in Fig. 5. Etchants which develop the retained austenite to this extent yield micrographs suitable for making quantitative measurements. Allten's reagent<sup>4</sup> is also very satisfactory for developing retained austenite as shown by Fig. 6. For simple structures, there is no particular advantage in using Allten's reagent. For more complicated structures containing smaller amounts of retained austenite it shows promise of being more satisfactory because, being used electrolytically, it can be controlled more effectively. It should be pointed out, however, that electrolytic etches may prove unsatisfactory for electron metallography because it has been found that a residue is sometimes left at phase boundaries. This residue is difficult to remove and often covers up much detail.

In structures containing more than two microconstituents it often becomes imperative to use a modified etchant. For example, Fig. 7 shows the microstructure of a specimen of S.A.E. 52100 steel etched in 2 pct nital. The undissolved carbide and tempered martensite are well developed, but there is no differentiation between the untempered martensite and retained austenite. When this structure is etched with 2 pct nital containing zephiran chloride, the complete structure as shown in Fig. 8 is developed.

In cases where it is not possible to develop the microstructure completely with a single etchant, a

composite etch (two etchants in succession) may be used. Such is the case with cemented carbide compositions containing both tungsten and tantalum carbide. An electrolytic alkaliferri cyanide etch (equal parts 10 pct potassium hydroxide and 10 pct potassium ferricyanide at 4 volts) develops only the angular shaped tungsten carbide grains. If an additional 3 pct nital is used after the above etch, the complete structure as shown in Fig. 9, is developed. The nital etch effectively reveals the smooth, round-contoured grains of tantalum carbide by attacking the cobalt binder.

When a satisfactory composite etch cannot be found, the only recourse is to use two or more etches independently. Such a procedure is not entirely satisfactory, but it is sometimes the only way to study the complete microstructure. For example, an electrolytic, 5 pct hydrochloric acid etch is effective in developing the secondary carbide precipitate in high temperature alloys. The primary carbide "aggregates," however, are either unattacked or etched so deeply that a faithful replica cannot be obtained, thereby precluding the possibility of interpreting the microstructure. On the other hand, a vacuum-cathodic etch<sup>5</sup> develops the structure of the primary carbide well as shown in Fig. 10. The secondary carbide particles which surround the primary carbide phase, however, are only faintly visible. Neither etchant is completely satisfactory, but the use of both permits a more accurate interpretation of the structure. In summary, results of the use of various etchants on typical metallographic specimens have been shown. From the results, it is evident that the success of a particular etchant in electron metallography cannot always be predicted from previous experience in light metallography. However, the etchants found to be satisfactory in light metallography should serve as starting points for the development of etchants more suitable for electron metallography.

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# Solubility of Gaseous Nitrogen in Gamma Iron and the Effect Of Alloying Constituents — Aluminum Nitride Precipitation

by L. S. Darken, R. P. Smith, and E. W. Filer

The solubility of nitrogen gas in purified iron and low alloy steels is determined for the  $\gamma$  region (930° to 1350°C). The diffusivity of nitrogen is estimated from the rate of approach to equilibrium. The investigation of aluminum-killed steels, held in nitrogen, discloses precipitation of aluminum nitride, the solubility of which is determined.

ALTHOUGH several investigations of the solubility of nitrogen gas in  $\gamma$  iron have been reported, all have made use of the method adopted by Sieverts in his classic work, whereby the solubility is determined by the pressure or volume change of the gas. The agreement between different investigators\* is rather poor, particularly as compared to the self-consistency of results of several individual investigators. The present report represents a portion of our investigation of the equilibrium of nitrogen and nitrogenous atmospheres with iron and steels. The method adopted in this temperature region (910° to 1400°C) consists of holding the specimen in gaseous nitrogen, quenching (or cooling), and determining the nitrogen content by direct analysis (solution in acid followed by distillation and titration of the ammonia).\*\*

Up to 1050°C a 20 in. vertical wire-wound (Kanthal) furnace was used; this was wound in three sections so that by proper adjustment of relative currents, and use of a modulator<sup>1</sup> and a commercial controller (using a chromel-alumel control couple), a zone almost 6 in. long could be maintained uniform within a few tenths of a degree. Since the temperature coefficient of the nitrogen solubility is low, the full precision was not utilized and a variation of 1° to 2° was tolerated; a variation of a similar amount also occurred occasionally between the beginning and end of the experiment. At higher temperature a vertically mounted, tubular Globar furnace and control unit was used; the zone of uniformity (1° to 2°C) was here limited to about 2 in.; fluctuations with time were comparable to those in the wire-wound furnace. Reported temperatures were measured by use of a platinum-platinum-rhodium thermocouple, which was frequently com-

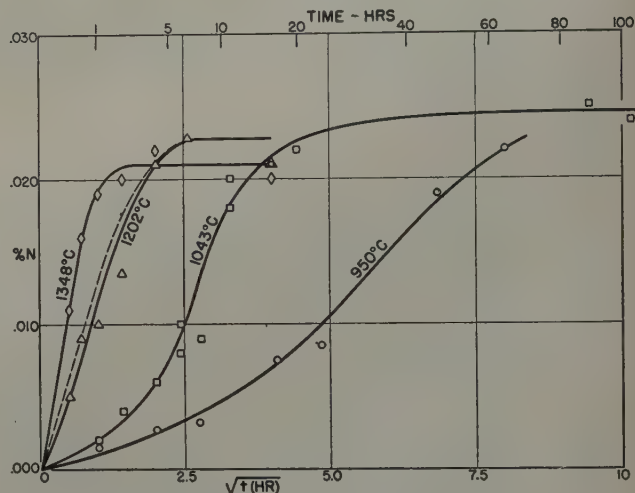


Fig. 1.—Nitrogen absorption as a function of time for electrolytic iron suspended in nitrogen gas (+1 pct  $H_2$ ). The dashed curve and that for 1348°C have the theoretical form for a diffusion controlled process with constant surface concentration.

pared with a similar standard couple which was calibrated at the gold and palladium points and also compared with one certified by the Bureau of Standards; error from this source is believed to be less than 1°C.

Nitrogen gas from a commercial cylinder was mixed with slightly over 1 pct H by use of a gas mixer described previously.<sup>2</sup> This mixture was passed over hot copper and through ascarite and phosphorus pentoxide to remove oxygen and water vapor. The purified gas contained 1.05 pct H. This procedure was adopted to prevent the formation on the specimens of oxide film, which is well known to be nearly impervious to nitrogen; its success was attested by

\* One of the difficulties of this method lies in the determination of the so-called "hot volume"—that is the amount of nitrogen (or other substance) in the gaseous phase. This subject was investigated and discussed by M. H. Armbruster, *Journal Amer. Chem. Soc.* (1943), 65, p. 1043.

\*\* The authors are greatly indebted to Glenn W. Momeyer for the analytical work of this investigation.

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Table I. Composition of Samples

| Iron or Steel | C     | Mn     | P     | S     | Si    | Al†    | N      |
|---------------|-------|--------|-------|-------|-------|--------|--------|
| 1*            | 0.011 | <0.001 |       |       | 0.008 | None   | <0.001 |
| 2*            | 0.012 | <0.001 | 0.004 | 0.003 | 0.002 | <0.001 | <0.001 |
| 3             | 0.10  | 0.41   | 0.011 | 0.024 | 0.01  | <0.001 | 0.003  |
| 4             | 0.10  | 0.44   | 0.010 | 0.024 | 0.01  | <0.001 | 0.003  |
| 5             | 0.10  | 0.44   | 0.011 | 0.023 | 0.01  | 0.005  | 0.003  |
| 6             | 0.10  | 0.42   | 0.011 | 0.025 | 0.01  | 0.013  | 0.003  |
| 7             | 0.75  | 0.55   | 0.025 | 0.032 | 0.020 | 0.038  |        |
| 8             | 0.10  | 0.43   | 0.10  | 0.025 | 0.01  | 0.047  | 0.004  |
| 9             | 0.051 | 0.35   | 0.006 | 0.033 | 0.006 | 0.054  |        |
| 10            | 0.79  | 0.62   | 0.011 | 0.025 | 0.023 | 0.062  |        |
| 11            | 0.10  | 0.44   | 0.012 | 0.023 | 0.01  | 0.144  | 0.004  |
| 12            | 0.064 | 0.26   | 0.052 | 0.023 | 0.21  |        |        |
| 13            | 0.073 | 0.28   | 0.020 | 0.022 | 0.57  |        |        |
| 14            | 0.074 | 0.28   | 0.012 | 0.015 | 1.26  |        |        |
| 15            | 0.052 | 0.24   | 0.010 | 0.015 | 2.55  |        |        |
| 16            |       |        |       |       | 3.5   |        |        |
| 17            | 0.028 | 0.24   | 0.010 | 0.013 | 4.8   |        |        |
| 18            | 0.10  | 0.43   | 0.010 | 0.034 | 0.007 |        |        |
| 19            | 0.10  | 0.53   | 0.010 | 0.043 | 0.006 |        |        |
| 20            | 0.20  | 1.46   | 0.027 | 0.022 | 0.205 |        |        |
| 21            | 1.40  | 12.98  | 0.048 | 0.019 | 0.32  | <0.001 |        |
| 22            |       | 0.028  | 0.014 | 0.029 | 0.003 |        | 0.0036 |

\* Irons 1 and 2 are carbonyl and electrolytic respectively. Spectrographic analysis indicated the presence of no other metallic elements in excess of 0.001 pct except for 0.02 pct Ni in each and 0.05 pct Cu in the electrolytic iron.

† Metallic aluminum; this is believed negligibly small in the steels which were not aluminum-killed and for which no value is tabulated.

the fact that specimens pulled up and cooled in the glass head of the furnace exhibited no tarnish except in the case of the high silicon steels. In this latter case a "getter" of transformer steel was ultimately suspended beneath the specimens. The purified gas was led through glass tubing (with two butt joints of treated rubber) and introduced into the porcelain furnace tube (¾ or 1 in. ID) through a mercury seal at the bottom. At the top was a ground pyrex joint, the male portion of which was sealed to the porcelain. The gas was discharged to the atmosphere through a long glass tube to prevent any breathing of air into the furnace. Although barometric readings were taken, these are not reported since the effect of departures from 760 mm was negligibly small. Similarly the effect of the 1 pct H on the nitrogen solubility is negligible; by Sievert's law

Table II. Solubility of N<sub>2</sub> in Purified Iron and Low Alloy Steels

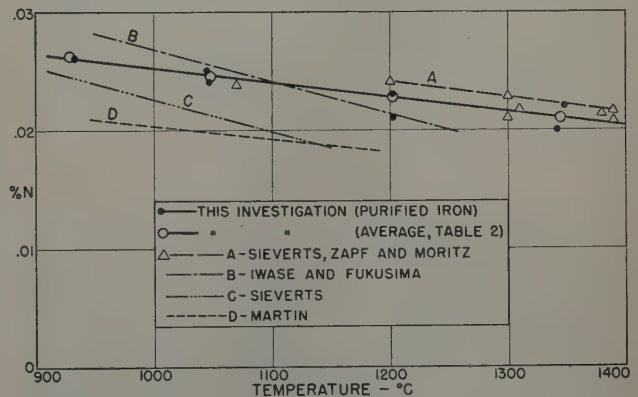
| Temperature, °C | Iron or Steel                         | Thickness, Mm | Time, Hr | Pct N              |
|-----------------|---------------------------------------|---------------|----------|--------------------|
| 933             | 1                                     | 0.34          | 16       | 0.026, 0.026       |
| 923             | 3                                     | 3.2           | 93       | 0.023              |
| 923             | 4                                     | 3.2           | 93       | 0.028              |
| 918             | 12                                    | 1.6           | 65       | 0.025              |
| 918             | 12                                    | 1.6           | 134      | 0.029              |
| 923             | Average of above                      |               |          | 0.026 <sub>2</sub> |
| 923             | solubility from smooth plot of Fig. 2 |               |          | 0.026 <sub>1</sub> |
| 1045            | 2                                     | 2.2           | 89       | 0.025              |
| 1047            | 2                                     | 2.2           | 68       | 0.024              |
| 1045            | 12                                    | 1.6           | 89       | 0.025              |
| 1047            | 12                                    | 1.6           | 68       | 0.023              |
| 1048            | 3                                     | 3.2           | 65       | 0.024, 0.025       |
| 1048            | 4                                     | 3.2           | 65       | 0.023, 0.027       |
| 1051            | 18                                    | 1.5           | 16       | 0.025              |
| 1051            | 19                                    | 2.0           | 16       | 0.024              |
| 1048            | Average of above                      |               |          | 0.024 <sub>5</sub> |
| 1048            | solubility from smooth plot of Fig. 2 |               |          | 0.024 <sub>6</sub> |
| 1202            | 2                                     | 2.2           | 6½       | 0.023              |
| 1203            | 2                                     | 2.2           | 16       | 0.021              |
| 1203            | 12                                    | 1.6           | 16       | 0.022              |
| 1200            | 3                                     | 1.6           | 16       | 0.024              |
| 1200            | 4                                     | 1.6           | 16       | 0.024              |
| 1202            | Average of above                      |               |          | 0.022 <sub>8</sub> |
| 1202            | solubility from smooth plot of Fig. 2 |               |          | 0.022 <sub>8</sub> |
| 1348            | 2                                     | 2.2           | 4        | 0.022              |
| 1342            | 2                                     | 2.2           | 16       | 0.020              |
| 1342            | 12                                    | 1.6           | 16       | 0.020              |
| 1348            | 3                                     | 1.6           | 16       | 0.021 <sub>5</sub> |
| 1348            | 4                                     | 1.6           | 16       | 0.021 <sub>5</sub> |
| 1345            | Average of above                      |               |          | 0.021 <sub>0</sub> |
| 1345            | solubility from smooth plot of Fig. 2 |               |          | 0.021 <sub>0</sub> |

this lowers the nitrogen solubility by only ½ pct—for example by 0.0001 pct out of 0.02 pct.

The composition of the irons and steels used is given in Table I. Except as noted below these were in sheet form; specimens were cut about ½ in. wide and 4 or 2 in. long, depending on the uniform zone of the furnace used. They were pickled and sanded. Several specimens were frequently run simultaneously; small porcelain rings were used as spacers in this case. The suspension wire was of iron. The series of aluminum steels were initially in bar form (¾ in. diam); half disks were used as specimens. The ingot iron used in an attempt to determine the diffusivity was a cylinder 4 in. long and ⅝ in. diam.

### Solubility of Nitrogen in $\gamma$ Iron

It was originally thought that the slow step in achieving equilibrium between specimen and atmosphere would be the diffusion of nitrogen through the specimen. It was hoped that both the solubility and the diffusivity could be determined by a time series. Electrolytic iron was used for this purpose and the results are shown in Fig. 1. Also shown in this figure is the form<sup>3, 4</sup> of the theoretical curve that would be expected if the surface of the specimen were saturated rapidly and remained so. The square root of time is used as abscissa in this figure to facilitate comparison with the theoretical curve (dashed) which is linear and of finite slope in the vicinity of

Fig. 2—The solubility of nitrogen gas (at atmospheric pressure) in  $\gamma$  iron.

the origin, becoming concave downward as saturation is approached, and eventually leveling off. At the lower temperatures the experimental data do not even approximate this form; the boundary condition is undoubtedly not satisfied and the diffusivity cannot reliably be computed from these data. It would seem that surface adsorption rather than diffusion is the slow step in attaining equilibrium. Even at 1200°C the same conclusions would seem to apply though to a lesser extent. This may be seen by comparison of the experimental data with the theoretical curve for diffusion into a slab under the condition of constant surface concentration. For the data at 1348°C, the curve in Fig. 1 is drawn with the theoretical form and corresponds to the diffusivity:

$$D = 3.1 \times 10^{-6} \text{ sq cm sec}^{-1}$$

These time series at least indicate the minimum time required for approximate equilibration. In each case, except for the lowest temperature, two specimens were run for a substantially longer time. At the lowest temperature a much thinner specimen was used to achieve equilibrium. The solubility of nitrogen gas in iron, as thus determined, is given in

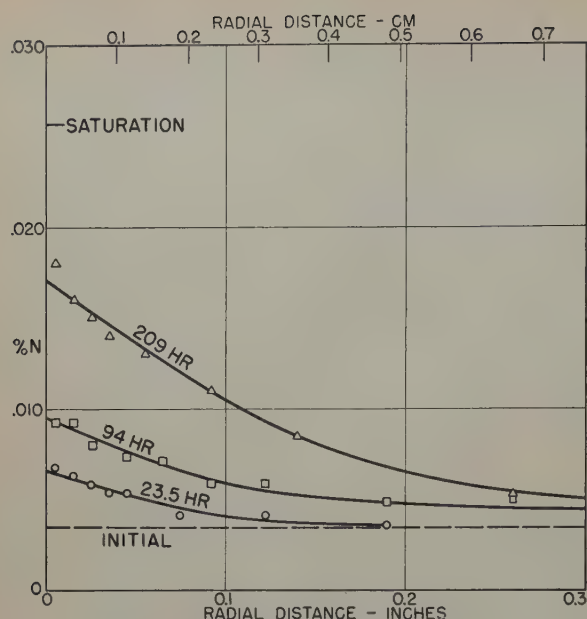


Fig. 3—Penetration curve for nitrogen in iron rod.

Table II. The solubility in several low alloy steels is also included. As indicated here and substantiated later, the extraneous constituents have a negligibly small effect; hence all these results at or near a given temperature are averaged. These averages, as well as the individual results for iron, are plotted in Fig. 2 and compared with the results of other investigators.<sup>5-8</sup> The results are represented remarkably well by a straight line, whose equation is:

$$[\text{Pct N}] = 0.0404 - 1.2 \times 10^{-5} T$$

#### Approximate Diffusivity at 955°C

In order to verify the previous conclusion that the slowness in the lower temperature region is due to failure to establish surface saturation and to determine the diffusivity, another series of experiments was run. An ingot iron cylinder (4 in. long, 5/8 in. diam) was suspended in the furnace in the same manner as before. After a predetermined time (23 1/2, 94, or 209 hr) the cylinder was quenched and subsequently turnings were taken on a lathe, after discarding the ends. The nitrogen content of the layers is shown in Fig. 3. It is quite apparent that the surface layer did not become saturated even in 209 hr. The diffusivity of nitrogen may be determined directly from its definition. By graphical integration the mean nitrogen content was computed for each time. The rate of entrance of nitrogen per unit area, as determined therefrom, divided by the concentration gradient (at the surface) at the corresponding time gives a mean:

Table III. Effect of Manganese on the Solubility of N<sub>2</sub> in Austenite

| Temperature, °C | Specimen No.  | Time, Hr | Pct Mn | Pct N              |
|-----------------|---------------|----------|--------|--------------------|
| 1051            | (From Fig. 2) |          | 0      | 0.024 <sub>7</sub> |
|                 | 18            | 16       | 0.43   | 0.025              |
|                 | 19            | 16       | 0.53   | 0.024              |
|                 | 20            | 6        | 1.46   | 0.025              |
|                 | 20            | 16       | 1.46   | 0.025              |
| 1203            | (From Fig. 2) |          | 0      | 0.022 <sub>7</sub> |
|                 | 21            | 16       | 12.98  | 0.046              |
| 1342            | (From Fig. 2) |          | 0      | 0.021              |
|                 | 20            | 16       | 1.46   | 0.020              |

Table IV. Effect of Silicon on the Solubility of N<sub>2</sub> in Austenite

| Temperature, °C | Specimen No.  | Time, Hr | Pct Si | Pct N              |
|-----------------|---------------|----------|--------|--------------------|
| 1046            | (From Fig. 2) |          | 0      | 0.024 <sub>5</sub> |
|                 | 12            | 89       | 0.20   | 0.025              |
|                 | 12            | 157      | 0.20   | 0.023              |
|                 | 13            | 89       | 0.58   | 0.023              |
|                 | 13            | 157      | 0.58   | 0.022              |
| 1203            | (From Fig. 2) |          | 0      | 0.022 <sub>5</sub> |
|                 | 12            | 16       | 0.20   | 0.022              |
|                 | 13            | 16       | 0.58   | 0.020              |
| 1342            | (From Fig. 2) |          | 0      | 0.021              |
|                 | 12            | 16       | 0.20   | 0.020              |
|                 | 13            | 16       | 0.58   | 0.018              |

$$D = 1.9 \times 10^{-7} \text{ sq cm sec}^{-1}$$

The same result was obtained using a more complicated method. The precision leaves much to be desired, but it is believed that the error probably does not exceed 20 pct.

#### Effect of Alloying Constituents

The effect on the solubility of nitrogen in austenite of the amounts of carbon, manganese, sulphur, and phosphorus usually present in plain low carbon steels is seen from Table II to be negligible. The effect of increasing amounts of manganese is shown in Table III. Up to 1.5 pct Mn, the effect is seen to be well within the error of analysis; from the previous data on time required (allowing for decreased thickness) as well as the agreement of the 6 and 16 hr specimens, there seems little doubt that these specimens were equilibrated with the atmosphere. The 13 pct Mn steel unquestionably absorbed considerably more nitrogen except at the highest temperature; no checks were run to determine whether it would have absorbed still more in longer time. Since 1.5 pct Mn does not observably affect the solubility and since

Table V. Nitrogen Absorbed by Aluminum-Killed Steels

| Temperature, °C | Specimen No.  | Thickness, Mm | Time, Hr | Pct Al | Pct N              |
|-----------------|---------------|---------------|----------|--------|--------------------|
| 1048            | (From Fig. 2) |               |          | 0      | 0.024 <sub>7</sub> |
|                 | 3             | 3.8           | 21       | <0.001 | 0.020              |
|                 | 3             | 3.8           | 65       | <0.001 | 0.024, 0.025       |
|                 | 4             | 3.8           | 21       | <0.001 | 0.019              |
|                 | 4             | 3.8           | 65       | <0.001 | 0.023, 0.027       |
|                 | 5             | 3.8           | 21       | 0.005  | 0.021              |
|                 | 5             | 3.8           | 65       | 0.005  | 0.024, 0.025       |
|                 | 6             | 3.8           | 21       | 0.013  | 0.021              |
|                 | 6             | 3.8           | 65       | 0.013  | 0.025, 0.027       |
|                 | 8             | 3.8           | 21       | 0.047  | 0.033              |
|                 | 8             | 3.8           | 65       | 0.047  | 0.048, 0.048       |
|                 | 11            | 3.8           | 21       | 0.144  | 0.045              |
|                 | 11            | 3.8           | 65       | 0.144  | 0.078, 0.082       |
| 1042            | 11            | (millings)    | 64       | 0.144  | 0.091, 0.092       |
| 1051            | 7             | 1.6           | 17       | 0.038  | 0.037              |
|                 | 7             | 1.6           | 40       | 0.038  | 0.038              |
|                 | 10            | 1.6           | 17       | 0.062  | 0.049              |
|                 | 10            | 1.6           | 40       | 0.062  | 0.051              |
| 1200            | (From Fig. 2) |               |          | 0      | 0.022 <sub>5</sub> |
|                 | 3             | 1.6           | 16       | <0.001 | 0.024              |
|                 | 4             | 1.6           | 16       | <0.001 | 0.024              |
|                 | 5             | 1.6           | 16       | 0.005  | 0.024              |
|                 | 6             | 1.6           | 16       | 0.013  | 0.023              |
|                 | 8             | 1.6           | 16       | 0.047  | 0.034              |
|                 | 11            | 1.6           | 16       | 0.144  | 0.073              |
| 1348            | (From Fig. 2) |               |          | 0      | 0.021 <sub>0</sub> |
|                 | 3             | 1.6           | 16       | <0.001 | 0.022              |
| 1350            | 4             | 1.6           | 16       | <0.001 | 0.021              |
|                 | 5             | 1.6           | 16       | 0.005  | 0.020              |
|                 | 6             | 1.6           | 16       | 0.013  | 0.020              |
|                 | 8             | 1.6           | 16       | 0.047  | 0.021              |
|                 | 11            | 1.6           | 16       | 0.144  | 0.031              |



the effect of high manganese appears to decrease with temperature, it was thought that there might be a nitride precipitate in the high manganese steel. However, metallographic examination disclosed a completely austenitic structure free of observable precipitate.

The effect of silicon on the solubility of nitrogen is shown in Table IV. At each temperature the nitrogen content was lowered slightly by silicon. Difficulty was experienced in equilibrating higher silicon steels with the nitrogen atmosphere; for example a specimen of a 1.2 pct Si steel (a member of the series tabulated) contained 0.016 pct N after 89 hr treatment at 1046°C, and a similar specimen contained only 0.009 pct N after the longer treatment of 157 hr. A dynamo grade steel (3.48 pct Si) behaved even more erratically. The highest nitrogen content attained was 0.012 pct at 1203°C; this steel, however, is partially ferritic. It seems probable that this difficulty is due to an oxide film in spite of the aforementioned precautions and the fact that such film was not directly observable in the case of specimens cooled in the head of the furnace. Such difficulty was avoided by using a higher hydrogen content and higher temperature, which procedure places the series in the  $\delta$  region beyond the range of the present report.

### Precipitation of Aluminum Nitride

To investigate the effect of small amounts of per cent Al, principal use was made of steels from a series of ingots from the same heat (Nos. 3, 4, 5, 6, 8, and 11 of Table I); the aluminum addition was 0,  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1, 2, and 4 lb per ton, respectively. A few other aluminum-killed steels were also used. The nitrogen content of all samples treated above 1000°C is given in Table V. Equilibrium is believed to have been substantially attained in at least one run for each specimen at each temperature. This statement is based on checks of shorter and longer time runs or comparison of the time requirement with Fig. 1 (noting agreement of shorter time runs), taking into account any difference in thickness and the extra nitrogen absorbed; millings were used in two cases to hasten equilibrium.

The equilibrium nitrogen content is plotted against aluminum in Fig. 4. At each temperature the nitrogen content was independent of aluminum up to a critical amount thereof, above which the nitrogen rose abruptly. The small amount of aluminum present would not in any case be expected to influence observably the solubility of nitrogen in homogeneous austenite; the behavior of the lower aluminum specimens particularly at higher temperature verify this expectation. The abrupt rise in nitrogen content at higher aluminum is typical of the behavior encountered in the case of a phase change. If such is the case then this straight rising line is a tie line connecting the compositions of the two phases in equilibrium and should have a slope equal to the ratio of nitrogen to aluminum in the new phase.<sup>†</sup> The observed slope corresponds, well within the experimental error,<sup>‡</sup> to a one to one atom ratio of nitrogen to aluminum. Since the only known nitride of aluminum<sup>9, 10</sup> corresponds to the chemical formula AlN,

<sup>†</sup> Strictly, the slope is the ratio of the difference of nitrogen and of aluminum in the two phases, but as both are so small in the austenite there is negligible error in the above statement.

<sup>‡</sup> The experimental error is believed to be principally in the analytical determination of aluminum. The analyses here reported and used were performed in this Laboratory, and the precision as judged by checks and prior experience is about 0.003 pct. Check analysis by an outside laboratory varied by twice this amount.

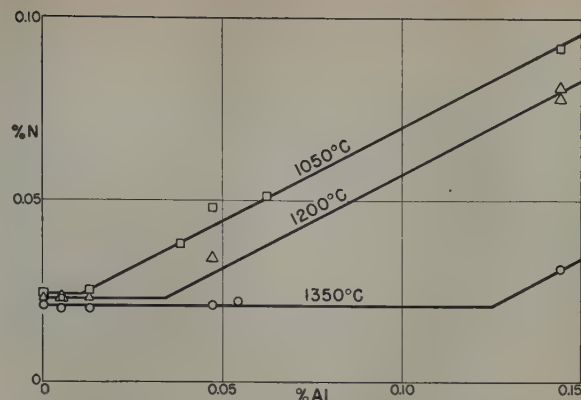
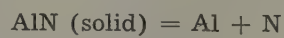


Fig. 4—Nitrogen content of aluminum-killed steels equilibrated with nitrogen gas.

it seems almost certain that it is the precipitation of this phase which gives rise to the nitrogen contents (Fig. 4) which are in excess of the solubility in austenite; the lines of the figure are drawn with this theoretical slope.

The equilibrium constant (solubility product) for the reaction:



may be determined from the position of the break in each curve of Fig. 4. This point corresponds to the composition of austenite in equilibrium with AlN. The values of  $K$  (which is [pct Al] [pct N]) thus found are plotted against the reciprocal of the absolute temperature in Fig. 5. The line drawn may be represented by the relation:

$$\log K = -\frac{7400}{T} + 1.95$$

The heat of formation of AlN from dissolved nitrogen and aluminum is thus found to correspond to  $\Delta H = -34,000$  cal. This heat may also be estimated from Kelley's compilation,<sup>9</sup> in which, for the formation of AlN from metallic aluminum and gaseous nitrogen,  $\Delta H$  is selected as  $-54,700$  cal (at 1200°C); the data reviewed exhibit discrepancies of over 10,000 cal. Subtracting from this  $\Delta H = -500$  cal for the solution of nitrogen gas in austenite, and  $\Delta H = -15,000$  for the solution of aluminum in ferrite<sup>11</sup> at 20°C (which is here considered to apply approximately to aluminum in austenite at 1200°C), the computed value for  $\Delta H$  of formation of AlN from aluminum and nitrogen dissolved in austenite is

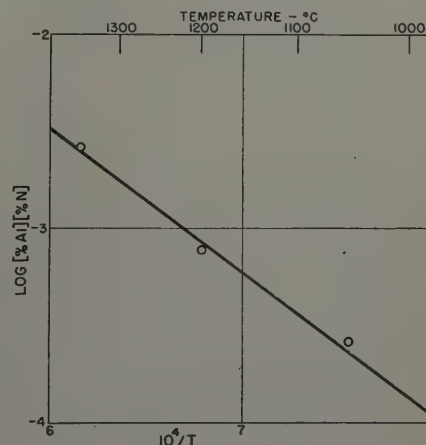


Fig. 5—The solubility product of aluminum nitride in  $\gamma$  iron.





Fig. 6—Aluminum-killed steel (0.144 pct Al) held in nitrogen for 93 hr at 923°C.

Aluminum nitride precipitate and grain refinement in rim zone permit its recognition even by naked eye. Rim-core boundary is indicated by arrows. Picral etch, X18.

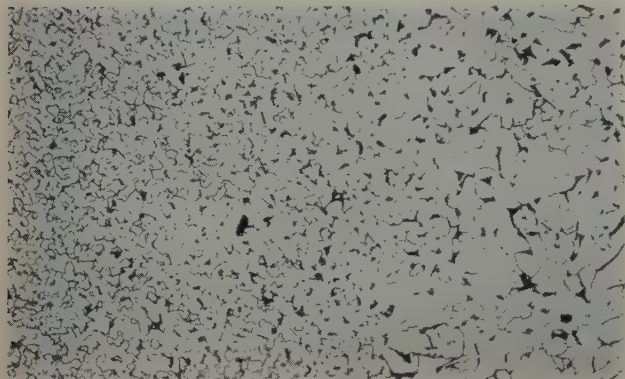
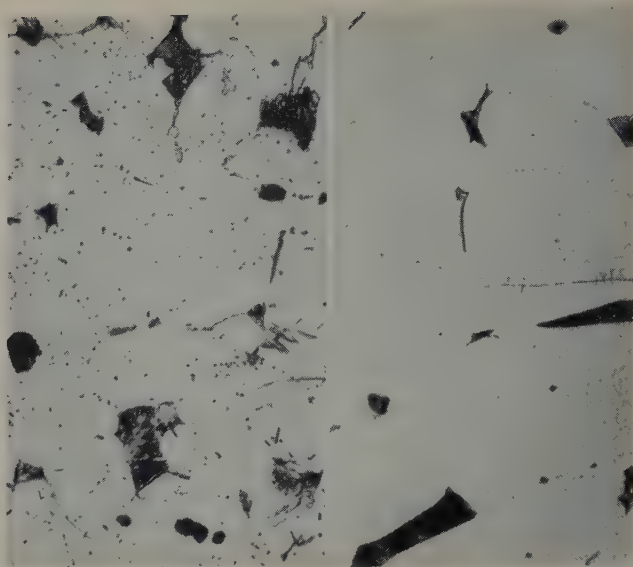


Fig. 7—Same specimen as Fig. 6. Rim-core boundary at X65.

found to be  $-39,200$  cal, as compared to the above experimental value of  $-34,000$  cal. The discrepancy is within the many errors involved in the two determinations and lends support to the foregoing general interpretation of our results.

Several of the specimens of Table V, as well as some treated at 923°C, were examined metallographically. Specimens containing 0.047 and 0.144 pct Al, for which the time of treatment at 923° and 1048°C was insufficient to achieve complete equilibrium, exhibit a definite "rim" and "core" which



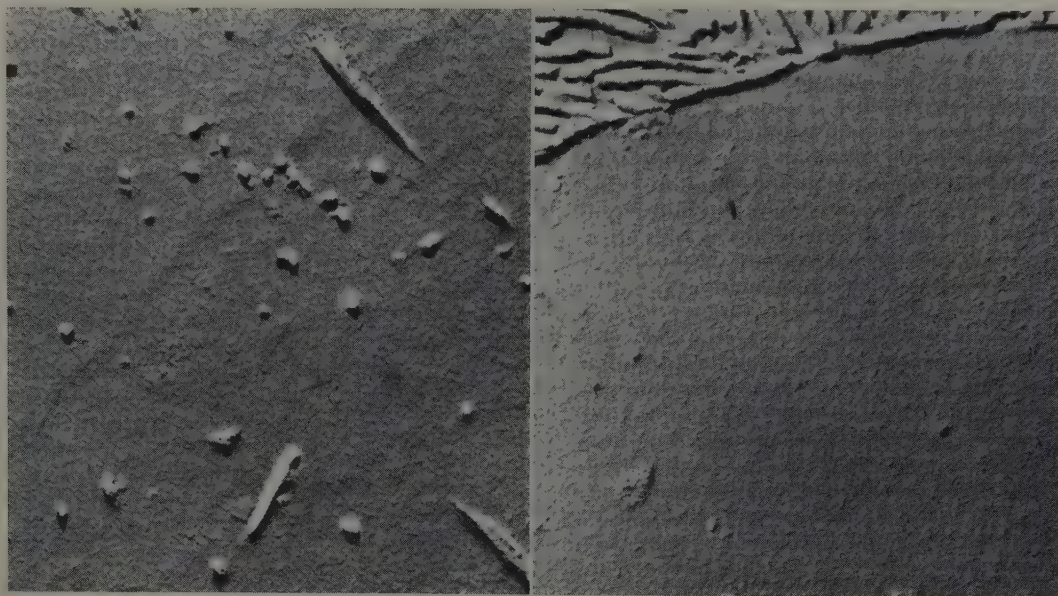
Rim

Core

Fig. 8—Same specimen as Fig. 6. Rim and core at X650.

were obvious, on the polished sample, even to the naked eye. Examination of the specimens disclosed that the rim differs from the core in two distinct respects: 1—the rim contains a copious fine precipitate which the core does not; 2—the ferrite grain size of the rim was considerably smaller (by about 2 A.S.T.M. sizes) than that of the core. Obviously, the nitride here forms a subscale similar to that found, for example, by Rhines<sup>12</sup> in the case of some oxides. The difference between the subscale (rim) and central (core) zones is illustrated for a typical specimen by the micrographs of Figs. 6 to 8. Even at X650 (Fig. 8) the precipitate is barely resolvable. However, it is shown clearly in the electron micrograph of Fig. 9.

Subscale thickness for a few specimens is given in Table VI. The fact that precipitation occurred throughout one specimen furnishes added evidence that this specimen (the composition of which is used in Fig. 4) is substantially equilibrated with the atmosphere. The final entry in the table is for a specimen in which the subscale has penetrated 90



Rim

Core

Fig. 9—Same specimen as Fig. 6. Electron micrograph at X9000 of rim showing aluminum nitride precipitate and core.



Table VI. Subscale Thickness

| Temperature, °C | Pct Al | Time of Treatment, Hr | Pct N | Subscale Thickness, Mm |
|-----------------|--------|-----------------------|-------|------------------------|
| 923             | 0.047  | 40½                   | 0.021 | 1.0                    |
|                 | 0.144  | 40½                   | 0.036 | 0.5 <sub>s</sub>       |
|                 | 0.144  | 93                    | 0.051 | 0.7 <sub>s</sub>       |
| 1048            | 0.047  | 21                    | 0.033 | 1.4 <sub>o</sub>       |
|                 | 0.047  | 65                    | 0.048 | (Complete)             |
|                 | 0.144  | 21                    | 0.045 | 0.65                   |
|                 | 0.144  | 65                    | 0.080 | 1.7 <sub>o</sub>       |

pct of the way to the center; this is in rough agreement with what would be expected by comparing its nitrogen content (0.080 pct) with that (0.091 pct) of the equilibrated milled specimen of Table V.

In general, the observed subscale thickness is somewhat less than the thickness computed from the diffusivity on the assumption that the surface of the specimen is saturated with nitrogen. This is not surprising since it has been shown, Fig. 3, that surface saturation is not achieved in this temperature range. It may be worthy of comment that in one case (the final entry of Table VI) the subscale or zone of precipitation extended much further than the zone of fine grains. This may be associated with the fact that aluminum nitride is by no means "insoluble" and hence the transition from rim to core is not sharp. Grain refinement undoubtedly depends on the number and size of the precipitated particles both of which vary somewhat. However, in all other cases, within the error of measurement, the grain size change occurred at the inner boundary of the subscale.

#### Summary

The solubility of nitrogen gas in iron and low alloy steels has been measured in the  $\gamma$  region from 930° to 1350°C. The specimens were equilibrated

with the gas and analyzed. The diffusivity of nitrogen in iron is reported at 955° and 1348°C ( $D = 1.9 \times 10^{-7}$  and  $3.1 \times 10^{-6}$  sq cm per sec, respectively). The solubility in plain low carbon steels is the same as that in iron and may be represented by the equation:

$$[\text{Pct N}] = 0.0404 - 1.2 \times 10^{-5} T$$

Manganese up to 1.5 pct has no observable effect. Silicon (0.58 pct) appears to lower the solubility slightly. Steels killed with sufficient aluminum exhibit a precipitate of aluminum nitride (AlN) which, for incompletely equilibrated specimens is in the form of a subscale. The solubility product of aluminum nitride has been determined. This solubility product or equilibrium constant may be represented by the relation:

$$\log K = \log [\text{Pct Al}] [\text{Pct N}] = -(7400/T) + 1.95.$$

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#### Technical Note

### Change in Yield Strength During Aging in Iron

by C. A. Wert

THE change in mechanical properties accompanying quench aging of carbon in  $\alpha$  iron has been known for a number of years. Since the amount of carbon involved is rather small, however, no measurements could be made to correlate the property change with the state of precipitation of the carbide. Indeed, until a few years ago it was not plain which property might be used to indicate the state of the progress of precipitation. Some years ago the internal friction of solid solutions of carbon in  $\alpha$  iron was demonstrated, and the use of this phenomenon to ascertain the amount of carbon in solid solution

at any given time was developed. Shortly afterward the author made a number of measurements in which changes in electrical resistance, thermoelectric emf, and hardness were determined simultaneously with the internal friction (and hence with the precipitation).<sup>1</sup> A little later Dijkstra and Wert measured the change in magnetic coercive force accompanying aging.<sup>2</sup>

The present work was undertaken to inquire into the changes in yield strength accompanying aging. The work was done on specimens made of Puron. These specimens were 0.05 in. in diam and about 6 in. long. Though specimens of this small size are not ideal for yield strength measurements, such specimens are desirable for internal friction meas-

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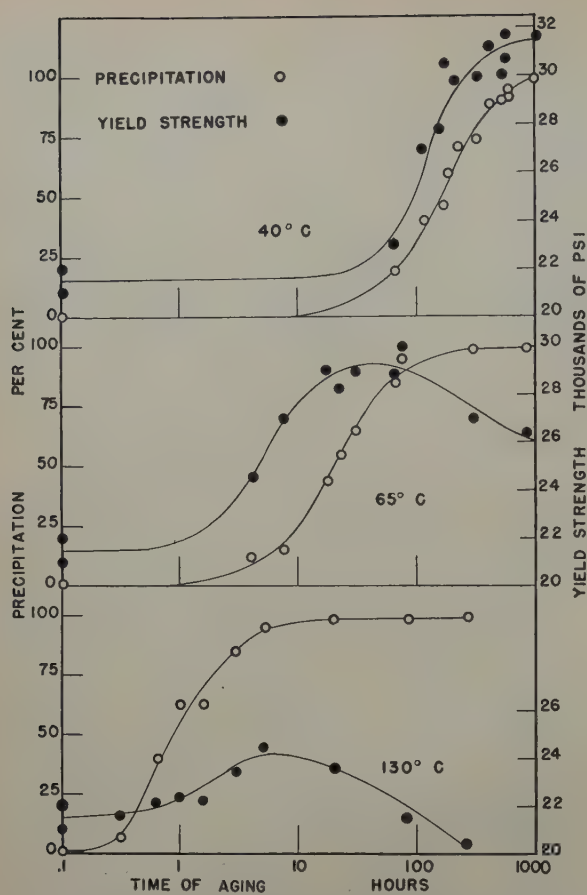


Fig. 1—Change in yield strength accompanying precipitation of carbide in  $\alpha$  iron.

urements. The tensile machine used was essentially the same as that used previously by the author in a similar type of investigation.<sup>8</sup> Specimen grips were made which would fit into both the torsion pendulum apparatus and the load bearing supports of the tensile machine. These grips were silver soldered to the ends of the specimen. Numerous attempts were made to attach the grips after all heat treatments (decarburization, carburization, and aging) just prior to the tensile measurement, but these attempts were all futile because the soldering operation invariably produced softening sufficient to cause failure of the sample at the grips. By soldering the grips in place before these heat treatments however, this was avoided except for an occasional sample which had a very high yield strength. Elongation of the sample during loading was measured by running a single strand of 0.001 in. resistance wire along a 2 in. section in the center of the sample. This strain-gage wire served as one arm of a Wheatstone bridge.

Measurements were made on three groups of samples; these groups were aged at 40°, 65°, and 130°C, respectively, after having been carburized to about 0.015 pct C. The yield strength data and the precipitation data (the latter as deduced from internal friction measurements) are shown in Fig. 1. The significant points to be noticed are:

Table I. Calculation of Particle Diameter for Fully Aged Specimens

| Temperature, °C | $d$ (Angstroms) | $d'$ (Angstroms) |
|-----------------|-----------------|------------------|
| 40              | 160             | 1000             |
| 65              | 210             | 1300             |
| 130             | 500             | 3000             |

1—The peak yield strength becomes higher as the aging temperature is lowered. This was perhaps to be expected from previous knowledge of behavior of hardness during quench aging.

2—The increase in yield strength occurs simultaneously with the precipitation. The peak is not reached until near the end of the precipitation process, after which the decline in yield strength is fairly rapid. Overaging is seen to manifest itself in yield strength just as it does in hardness. It is not clear from these measurements (nor does it seem clear from any other measurement) what is the detailed mechanism of overaging.

By methods previously described,<sup>1</sup> a calculation of particle diameter,  $d$ , for fully aged specimens (and hence of mean particle distance,  $d'$ ) was made.<sup>1</sup> These calculations give the results shown in Table I.

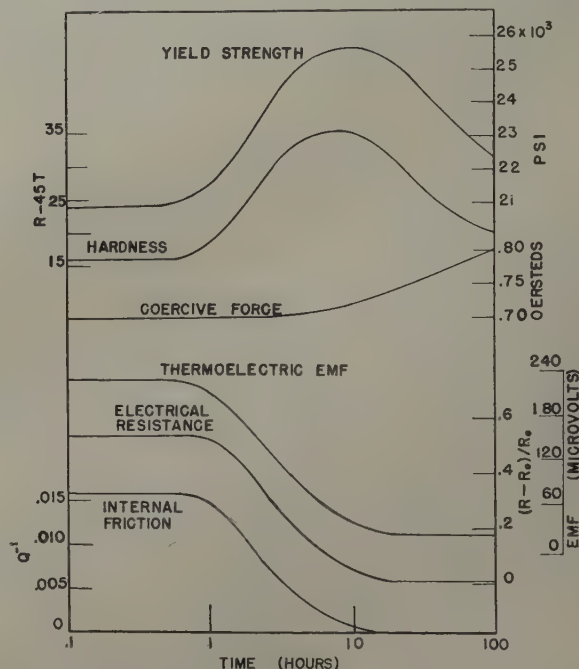


Fig. 2—Change in various properties during aging of carbon in iron at 100°C.

This plot represents yield strength, hardness, and coercive force measurements at 20°C; internal friction at 40°C; electrical resistance at -195°C; and thermoelectric emf (relative to decarburized iron) between -195° and 0°C.

If the peak yield strength be plotted as a function of  $\log d'$  (after Gensamer, Pearsall, Pellini, and Low<sup>4</sup>) a straight-line function is obtained though with a much different magnitude and slope from the work of Gensamer et al.

This measurement adds to the growing list of physical properties that have been correlated to the precipitation of carbide in  $\alpha$  iron. Fig. 2 shows schematically how these properties change during a typical heat treatment at, say, 100°C. With the exception of magnetic coercive force, where a striking critical-size-effect was observed, all these properties change steadily during the precipitation, the major change in property coming during the most rapid formation of the carbide.

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# Effect of Varying the Rate of Reduction on the Magnetic Properties, Ultimate Tensile Strength, and Resistivity Of 18/8 Stainless Steel Wire

by Samuel Storchheim

IT was noted that variations existed in the magnetic properties, namely, coercive force,  $H_c$ , and remanence,  $B_r$ , of 18/8 stainless steel wires of the same analysis when these wires were given the same percentage of reduction of area at different rates of reduction. In order to determine the extent of these variations, a program was initiated whereby commercial 302 and 304 stainless steels were drawn with a wide variation of speeds. Ultimate tensile strengths and specific resistances, as well as the  $H_c$ - $B_r$  measurements, were determined. If variations of considerable magnitude were found, it was thought that the knowledge accrued from the investigation could probably aid in determining the particular drawing speed required to obtain desired properties for a given specification for a particular analysis of wire.

## Drawing Procedure

Two specimens (set I, No. 302 and No. 304), the chemical analyses of which are given in Table I, were drawn at different speeds, namely, 45 to 3900 ft per min, directly from 0.016 in. diam wire to 0.004 in. diam wire, a 93.7 pct reduction of area. To obtain this high percentage of reduction, the wire at 0.016 in. was softened by annealing at 1150°C. It was then strung in a No. 16CF variable speed Vaughn drawing unit and passed through 13 B.&S. gage dies of successively smaller diameter, as shown in the accompanying table.

Following this step, several hundred feet of the wire was drawn, at a particular speed, through the dies and wound upon a spool. Once the sample of wire was drawn at the desired speed, the spool with the finished sample was removed, tagged for later identification, and an empty spool was placed in the machine. Another wire sample was drawn at a different speed, after making the necessary adjustments upon the Vaughn unit. At the greater speeds, several thousand feet of sample were drawn to insure that the wire to be used for testing would be uniform. This was done because the desired speed was not reached instantly; the wire taking a short while to attain the required drawing rate. All speed measurements were made by placing a tachometer against one of the machine's pulleys during the actual drawing of the specimens.

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To broaden the extent of the investigation, two additional specimens (set II, No. 302 and 304), analyses for which are given in Table I, were studied for variations in properties. However, these were drawn at heavier starting sizes directly through nine dies in a 12 HF Vaughn wire drawing unit. The B.&S. gage numbers and die diameters used were as given in the accompanying table which shows an

| Set I, No. 302 and 304 |               | Set II, No. 302 and 304 |               |
|------------------------|---------------|-------------------------|---------------|
| B.&S. No.              | Die Diam, In. | B.&S. No.               | Die Diam, In. |
| 26                     | 0.0159        | 13                      | 0.072         |
| 27                     | 0.0142        | 14                      | 0.064         |
| 28                     | 0.0126        | 15                      | 0.057         |
| 29                     | 0.0113        | 16                      | 0.051         |
| 30                     | 0.010         | 17                      | 0.045         |
| 31                     | 0.0089        | 18                      | 0.040         |
| 32                     | 0.008         | 19                      | 0.036         |
| 33                     | 0.0071        | 20                      | 0.032         |
| 34                     | 0.0063        | 21                      | 0.0285        |
| 35                     | 0.0056        |                         |               |
| 36                     | 0.005         |                         |               |
| 37                     | 0.0045        |                         |               |
| 38                     | 0.004         |                         |               |

84.4 pct reduction of area. The 0.072 in. diameter wire was also annealed at 1150°C. The process of obtaining samples was the same as described above. The only difference between the two was that the rates involved were not as extensive, set II covering a range of 625 to 1150 ft per min.

Tensile tests were carried out for the 0.004 in. diam wires on a horizontal Scott Tensile Tester, while tensile tests for the 0.028 in. diam wires were made on a vertical Scott Tensile Tester. Each value listed in the tables represented the average of five samples with a maximum deviation of approximately 3 pct among the samples. Resistance per foot of the wires was determined by use of standard bridges accurate to the nearest hundredth of an ohm for the 0.004 in. wire, and to the nearest thousandth of an ohm for the 0.028 in. wire. The resistances per foot were then converted to resistivities by use of the following equation:

$$P = R \times CM$$

where  $R$  is the resistance per ft in ohms per ft;  $CM$ , the area in circular mils; and  $P$ , the resistivity in ohms- $CM$ . The values listed in the tables likewise

ft

represented the average of five samples among which there was a maximum deviation of about 2 pct.

The magnetic measurements,  $H_c$ - $B_r$ , were made with a Hysteresis Loop Tester<sup>1</sup> which projected the

<sup>1</sup> W. W. Wetzel: Review of the Present Status of Magnetic Recording Theory. Part I. *Audioengineering* (November 1947) 31, No. 10.

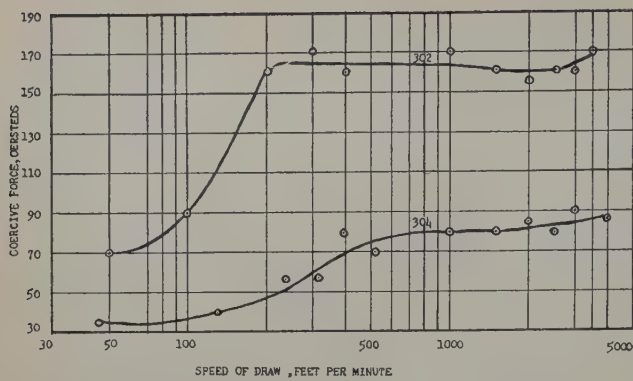


Fig. 1—Coercive force as a function of speed of draw for set I.

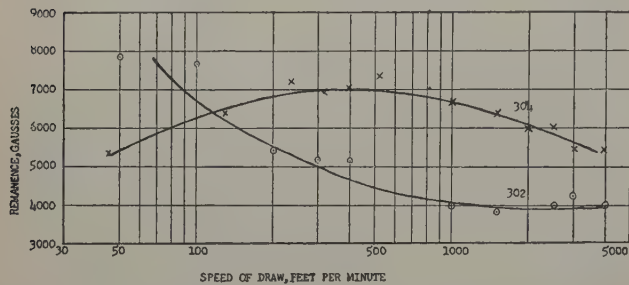


Fig. 2—Remanence as a function of speed of draw for set I.

image of the hysteresis loop on a previously calibrated cathode ray oscilloscope screen. The results obtained were the average of five samples with a maximum deviation of 5 pct for the  $H_c$  readings and 10 pct for the  $B_r$  readings.

The data obtained using these sets of stainless steel types are tabulated in Tables II to V, and from these tables curves were drawn depicting the general nature of the various relationships between the log of the rate of reduction vs. other properties, Figs. 1 to 4.

### Discussion of Results

**Rate of Reduction vs. Coercive Force:** For set I, the two analyses exhibited similar coercive force curves with the exception that they were displaced from each other, see Fig. 1. For the 302 analysis, the curve indicated that the  $H_c$  values were low at low rates of draw, but rose quickly at moderate rates of

draw to a value approximately 143 pct greater than that initially obtained. Once this "ultimate" value was obtained, there was little deviation from it except that caused by scatter. The 304 curve showed an initially lower  $H_c$  value than the 302 curve at low speeds. This value also rose as did the 302 curves, but more slowly. As in the case of the 302 curve, the final  $H_c$  of the 304 curve increased over its initial value by approximately 143 pct.

The limited spread of rates of reduction for set II did not warrant a similar plotting. However, these data plus those of set I indicated that an increase in the percentage of nickel content caused an upward displacement in the relative positions of curves; i.e., the  $H_c$  was increased for the same speed of draw when the nickel content was higher.

**Rate of Reduction vs. Remanence:** When the remanence curves for the two analyses of set I were plotted, they did not follow similar patterns as was the case with the coercive force curves, see Fig. 2. The 302 curve indicated a high  $B_r$  value at low drawing speeds which gradually fell off at increasing speeds and then levelled off at high rates of draw and remained relatively constant as in the case of the  $H_c$  values. The 304 curve behaved differently in that the initial values of  $B_r$  at low drawing rates were low. As the rates increased these values increased and then decreased gradually.

The data from set I together with that from set II indicated that higher nickel contents at moderate-to-fast rates of draw exhibited lower values of  $B_r$ . However, set I showed that the higher nickel 302 at slow rates of draw exhibited values of  $B_r$  about 45 pct greater than the lower nickel 304, in fact 9 pct higher than any other obtained with the lower nickel analysis regardless of drawing speed. The variation of  $B_r$ , within the higher nickel (set I, 302) specimens, was greater over the range of drawing speeds investigated than the lower nickel (set I, 304), namely, 51.0 pct as against 27.2 pct, respectively.

**Rate of Reduction vs. Ultimate Tensile Strength:** Plotting the ultimate tensile strengths of both the 302 and 304 vs. the rate of reduction gave two curves similar in appearance, but, as in the  $H_c$  set, dis-

Table I. Analyses of Stainless Steels Used, Pct

|        | Type | C     | Mn   | P     | S     | Si   | Mo   | Ni   | Cr    |
|--------|------|-------|------|-------|-------|------|------|------|-------|
| Set I  | 302  | 0.08  | 0.91 |       |       | 0.59 | 0.08 | 9.41 | 18.39 |
|        | 304  | 0.070 | 1.07 | 0.030 | 0.018 | 0.40 | 0.19 | 8.47 | 18.91 |
| Set II | 302  | 0.12  | 1.50 | 0.025 | 0.019 | 0.70 |      | 9.40 | 18.04 |
|        | 304  | 0.071 | 0.97 | 0.034 | 0.030 | 0.45 | 0.25 | 9.85 | 18.04 |

Table II. Set I, 302

| No. | Rate of Reduction, Ft per Min | $H_c$ , Oersted | $B_r$ , Gausse | Ultimate Tensile, 10 <sup>3</sup> Psi | Resistivity, Ohm-cm per Ft |
|-----|-------------------------------|-----------------|----------------|---------------------------------------|----------------------------|
| 1   | 50                            | 70              | 7850           | 395                                   | 555                        |
| 2   | 100                           | 90              | 7700           | 325                                   | 540                        |
| 3   | 200                           | 160             | 5450           | 372                                   | 500                        |
| 4   | 300                           | 170             | 5180           | 369                                   | 500                        |
| 5   | 400                           | 160             | 5180           | 372                                   | 500                        |
| 6   | 1000                          | 170             | 4000           | 372                                   | 490                        |
| 7   | 1500                          | 160             | 3850           | 369                                   | 500                        |
| 8   | 2000                          | 155             | 4250           | 356                                   | 510                        |
| 9   | 2500                          | 160             | 4000           | 365                                   | 500                        |
| 10  | 3000                          | 160             | 4250           | 372                                   | 490                        |
| 11  | 3900                          | 170             | 4000           | 372                                   | 485                        |

Table III. Set I, 304

| No. | Rate of Reduction, Ft per Min | $H_c$ , Oersted | $B_r$ , Gausse | Ultimate Tensile, 10 <sup>3</sup> Psi | Resistivity, Ohm-cm per Ft |
|-----|-------------------------------|-----------------|----------------|---------------------------------------|----------------------------|
| 1   | 45                            | 35              | 5330           | 372                                   | 615                        |
| 2   | 130                           | 40              | 6400           | 357                                   | 610                        |
| 3   | 235                           | 55              | 7200           | 361                                   | 600                        |
| 4   | 315                           | 55              | 6930           | 361                                   | 595                        |
| 5   | 395                           | 80              | 7070           | 357                                   | 585                        |
| 6   | 510                           | 70              | 7330           | 357                                   | 590                        |
| 7   | 1000                          | 80              | 6670           | 357                                   | 580                        |
| 8   | 1500                          | 80              | 6400           | 357                                   | 570                        |
| 9   | 2000                          | 85              | 6000           | 350                                   | 560                        |
| 10  | 2500                          | 80              | 6000           | 357                                   | 560                        |
| 11  | 3000                          | 90              | 5460           | 357                                   | 555                        |
| 12  | 3900                          | 85              | 5460           | 357                                   | 555                        |

Table IV. Set II, 302

| No. | Rate of Reduction, Ft per Min | $H_c$ , Oersted | $B_r$ , Gausse | Ultimate Tensile, 10 <sup>3</sup> Psi | Resistivity, Ohm-cm per Ft |
|-----|-------------------------------|-----------------|----------------|---------------------------------------|----------------------------|
| 1   | 625                           | 220             | 1290           | 271                                   | 465                        |
| 2   | 710                           | 220             | 1270           | 279                                   | 460                        |
| 3   | 815                           | 210             | 1450           | 279                                   | 460                        |
| 4   | 885                           | 195             | 350            | 275                                   | 475                        |
| 5   | 1000                          | 240             | 2090           | 268                                   | 470                        |
| 6   | 1120                          | 220             | 2560           | 270                                   | 465                        |



placed from each other, see Fig. 3. Initially, the values were high at slow drawing rates but decreased gradually to a value which remained relatively constant from moderate to very fast drawing rates; i.e. constant from about 200 ft per min up to 3900 ft per min. The maximum decrease in tensile strength obtained at fast rates of draw for the "constant" tensile value over the initially high (slowest speed of draw) value was approximately 6 pct for the 302 and 4 pct for the 304. In the cases investigated the higher carbon 302 specimen of both sets I and II exhibited the higher tensile values, about 4 pct higher for set I and 10 pct higher for set II. The low carbon content 304 tensile value at 50 ft per min was equivalent to the higher carbon containing 302 drawn between 300 and 3900 ft per min. The low tensile value obtained for the 302 curve at 100 ft per min was believed caused by a possible improper sampling; i.e., sufficient wire may not have been drawn to obtain a true representation of that particular drawing speed. The "dips" in the two curves at 2000 ft per min possibly were the results of a mechanical fluctuation of the drawing unit while the wire was being drawn.

**Rate of Reduction vs. Resistivity:** The resistivity/rate curves generally were not too alike except that they showed a trend to decrease as the speed increased, see Fig. 4. For the 302 curve of set I, the strongly decreasing trend stopped at about 300 ft per min where the resistivity partially levelled off to a slowly decreasing value. Between 50 to 300 ft per min a maximum drop of 10 pct was experienced. The curve for 304 of set I showed a gradual decrease through the entire range of speeds investigated. The maximum decrease in resistivity obtained again was about 10 pct. In both sets of curves, the highest values of resistivity were found at the slowest drawing speeds.

Using both groups of data from sets I and II, it was seen that the resistivities were lowered by an increase in nickel content; i.e., for the same rate of drawing speed, an analysis of higher nickel content exhibited a lower specific resistance. The lower nickel 304 curve of set I at very slow rates of draw exhibited a value of resistivity approximately 10 pct greater than the higher nickel 302 for the same low rate of draw, namely, 50 ft per min. A maximum difference of almost 20 pct was obtained between the two analyses over the range of speeds investigated.

### Explanation of Effects of Drawing Speed

A possible explanation of the effects found on the properties of 18/8 stainless steel by varying the rate of drawing speed could be as follows: Cold working a metastable austenitic 18/8 stainless steel produces martensite, provided the temperature during work-

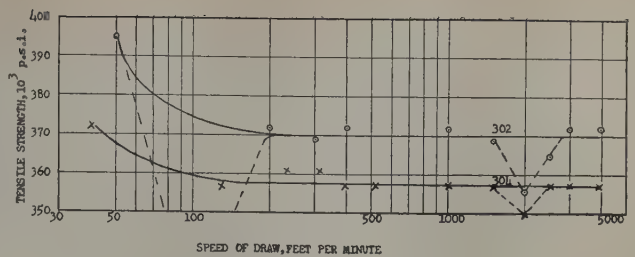


Fig. 3—Ultimate tensile strength as a function of speed of draw for set I.

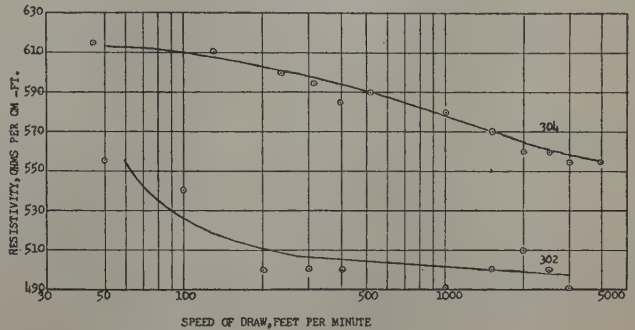


Fig. 4—Resistivity as a function of speed of draw for set I.

ing is not much higher than room temperature.<sup>2</sup> During the process of drawing wire through a die or a series of dies, an increase in temperature of the wire occurs, because of the dual processes of deformation and friction. The wire generally will be cooled off by the coolant to approximately room temperature in the time that it travels the distance from one die to the next. Should the temperature become greater, less martensite will be formed. Thus, if the speed of draw is increased to the point where the lubricant can no longer cool the wire fast enough, the temperature of the wire will rise above the room temperature. Therefore, the higher the drawing speed, the higher the temperature, and less martensite will be formed; consequently, the *Br*, resistivity, and tensile strength will be lower and the *Hc* will be higher.

### Conclusion

It was determined that variations did exist in magnetic properties, ultimate tensile strength, and specific resistance of commercial 18/8 stainless steel wires when the rate of reduction of these wires was varied. With increasing drawing rates it was found that coercive force increased, while remanence, tensile strength, and resistivity decreased. The changes in coercive force and remanence were quite extensive, while those of tensile and specific resistance, although significant, were less. A higher nickel content caused, for the same rate of draw, an increase in *Hc* and a decrease in *Br* and resistivity. Higher carbon contents exhibited higher tensile values for the same rate of draw.

From the above results and by possible further future investigation, it would appear that an 18/8 stainless steel analysis, which might normally have been considered inferior for a particular specification, could be salvaged by the correct choice of drawing speed. This could be of special value when the present critical situation regarding the availability of almost all metals and alloys is considered.

### Acknowledgment

The author should like to express his appreciation to the Wilbur B. Driver Co. for permission to publish this article.

<sup>2</sup> Thum: *Book of Stainless Steels*. A.S.M., Cleveland.

Table V. Set II, 304

| No. | Rate of Reduction, Ft per Min | Hc, Oersted | Br, Gausse | Ultimate Tensile, 10 <sup>3</sup> Psi | Resistivity, Ohm-cm per Ft |
|-----|-------------------------------|-------------|------------|---------------------------------------|----------------------------|
| 1   | 630                           | 250         | 1440       | 251                                   | 455                        |
| 2   | 740                           | 235         | 1130       | 251                                   | 450                        |
| 3   | 815                           | 255         | 1130       | 248                                   | 445                        |
| 4   | 915                           | 240         | 1270       | 251                                   | 455                        |
| 5   | 1050                          | 240         | 1440       | 237                                   | 455                        |
| 6   | 1150                          | 235         | 1270       | 253                                   | 450                        |

# Correlation Between Electrical Conductivity and Temperature

## Coefficient of Resistance of Solid-Solution Alloys

by M. Hansen, W. R. Johnson, and John M. Parks

AS part of a research project sponsored by the Signal Corps Engineering Laboratories, which had the objective of obtaining a magnet wire of good conductivity and low temperature coefficient of resistance, a comprehensive literature survey, supplemented by experimental work, revealed that a linear relationship exists for solid-solution alloys between the electrical conductivity,  $\kappa$ , and the temperature coefficient,  $\alpha$ , as expressed by the equation:

$$\kappa = \alpha\beta$$

where  $\beta$  is constant for the solvent metal and  $\alpha = \frac{\Delta R}{\Delta t R_0}$  per °C.

It has long been known that the electrical conductivity at a given temperature and the temperature coefficient of resistance of binary alloys are related to their constitution by the LeChatelier-Guertler rules, as illustrated by Figs. 1 and 2:

Rule 1—In alloy systems consisting of a heterogeneous mixture of two phases, the electrical conductivity and temperature coefficient vary as a straight line, if the composition of the alloys is given in volume percentage, Fig. 1.

Rule 2—In solid solutions, the electrical conductivity and temperature coefficient are always lower

than those of the solvent metal, and usually a considerable decrease occurs with the first small percentage additions of the solute metal, Fig. 2b. If the two components form a continuous series of solid solutions, the electrical conductivity and temperature coefficient curves take the form of a U-curve, Fig. 2a.

That some kind of proportionality exists between electrical conductivity and temperature coefficient of resistance is implied by the LeChatelier-Guertler rules and by study of data such as those given by Smith and Palmer,<sup>1</sup> Fig. 3. Dellinger<sup>2</sup> in 1910 first recognized this relationship in a number of commercial copper wires, ranging in conductivity from 94 to 100.7 pct I.A.C.S. He gave the ratio of temperature coefficient to the percentage of conductivity as a constant,  $C = 0.003939$ . A year later, Lindeck<sup>3</sup> observed that the linear relationship was valid for a wider range of conductivity in "various sorts of copper," and concluded that the product of resistivity and temperature coefficient was  $6.78 \times 10^{-5} \pm 1.5$  pct. Since then, this relationship seems to have been entirely ignored.

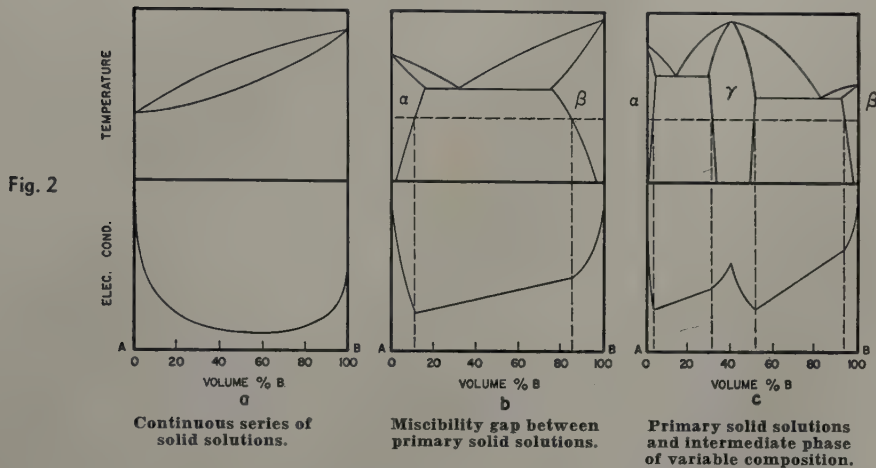
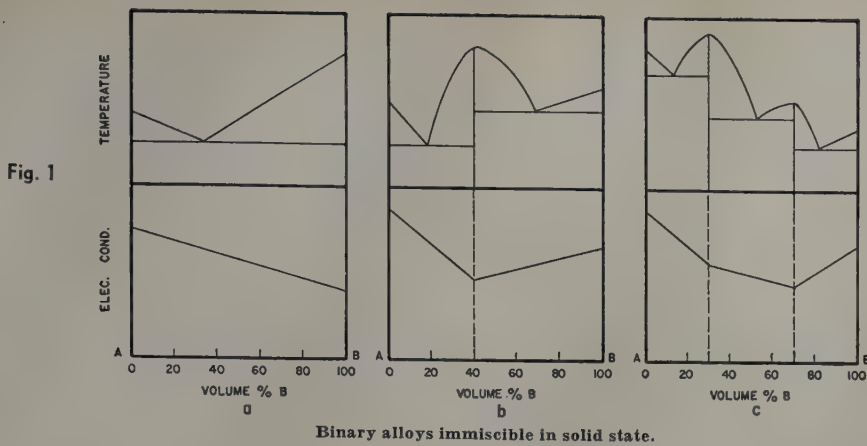
### Conductivity-Temperature Coefficient Relationship

If the electrical conductivity of copper solid-solution alloys with phosphorus, silicon, arsenic, antimony, aluminum, nickel, manganese, and iron is plotted against the temperature coefficient of these alloys, the diagrams in Figs. 4 and 5 are obtained. Similar data were found with copper-rich solid solutions containing magnesium, cobalt, and titanium,<sup>13</sup> as shown in Fig. 6. In all cases, a linear relationship exists. The point representing the highest

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Discussion on this paper, TP 3189E, may be sent, 2 copies, to AIME by April 1, 1952. Manuscript, July 12, 1951. New York Meeting, February 1952.





Figs. 1 and 2—Electrical conductivity of binary alloy vs. constitution.

conductivity and temperature coefficient is that of pure copper; as increasing percentages of solute elements are added, both the electrical conductivity and the temperature coefficient of resistance decrease along the straight line, until the solubility limit is reached. Beyond that composition, a deviation from the straight line results as illustrated by the Cu-P and Cu-Al data presented in Figs. 4 and 5.

If the low conductivity end of these plots is examined in detail, it may be seen that, in the case of the solid solutions with phosphorus, arsenic, and antimony, the extrapolated line almost intersects the origin of the plot. With Cu-Si and Cu-Al solid solutions, the straight line cuts the abscissa slightly to the right of the origin; whereas with Cu-Ni, Cu-Mn, and Cu-Fe, it cuts the abscissa to the left of the origin, nickel, manganese, and iron being transition elements. However, with all of these addition agents to copper, there is no appreciable deviation from the straight line conductivity vs. temperature coefficient of resistance relationship except for the low conductivity, low temperature coefficient range of Cu-Mn and Cu-Ni solid solutions. In Cu-Mn solid solutions, a negative temperature coefficient of resistance is reached between 4.5 and 9.5 pct Mn, Fig. 3.

Copper and nickel form a continuous series of solid solutions. According to Feussner and Lindeck,<sup>21</sup> the temperature coefficient becomes negative between 30 and 40 pct Ni and, with increasing nickel contents, positive again between 46 and 49 pct Ni. This finding agrees with that of Smith and Palmer, Fig. 3, who found that a negative temperature coefficient will be attained at about 33 pct Ni. On the

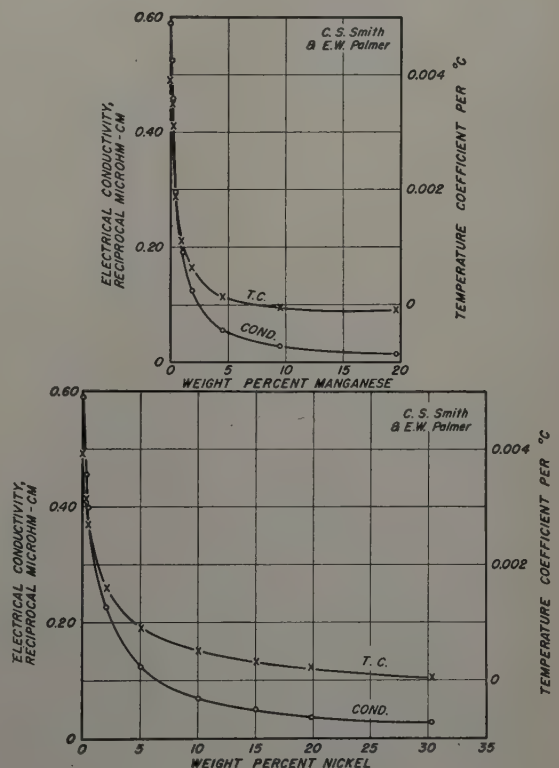


Fig. 3—Electrical conductivity and temperature coefficient of resistance of Cu-Mn and Cu-Ni solid solutions.

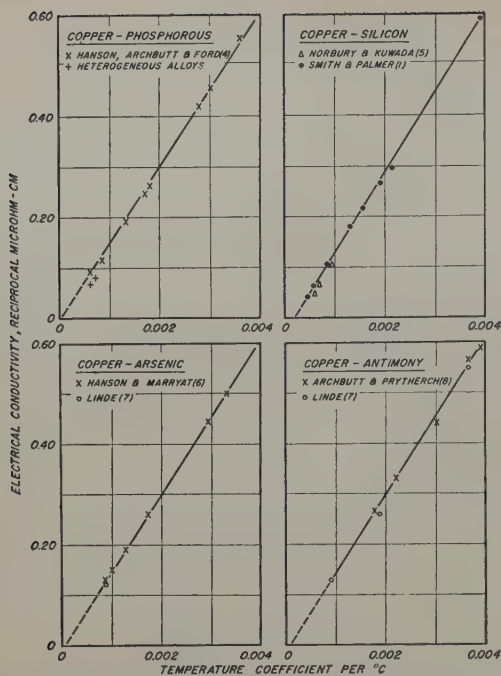


Fig. 4—Electrical conductivity vs. temperature coefficient of resistance of solid solutions of copper with phosphorus, silicon, arsenic, and antimony.

other hand, Krupkowski<sup>10</sup> found a negative temperature coefficient around 45 pct Ni. As the nickel content is increased further, the conductivity vs. temperature coefficient plot follows a curve which approaches the point representing pure nickel ( $\kappa_{20^\circ\text{C}} = 14.62$ ;  $\alpha_{0-100^\circ\text{C}} = 0.0069$ ).<sup>14</sup> As shown in Fig. 5, this curve is not a straight line, probably because alloys with more than 69 pct Ni are ferromagnetic at room temperature. The temperature coefficient curve for the Cu-Ni system, as determined by Krupkowski,

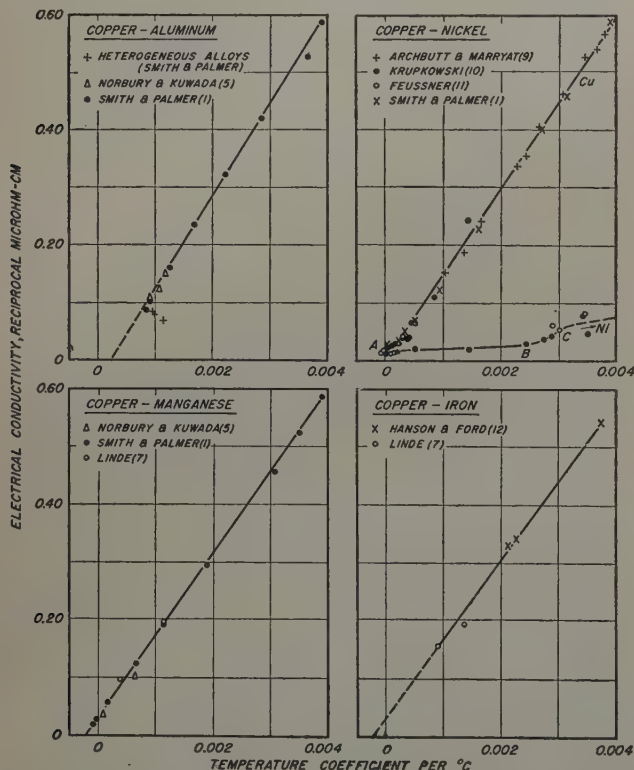


Fig. 5—Electrical conductivity vs. temperature coefficient of resistance of solid solutions of copper with aluminum, nickel, manganese and iron.

shows a large deviation from the ideal U-curve in this composition range, which indicates that the temperature coefficient is considerably affected by the electronic transitions which produce ferromagnetism.

Fig. 6 summarizes the data on various copper-base solid solutions plotted on the same basis; it indicates a slight spread in the data for these alloys. This linear relationship also holds for ternary copper-base solid solutions, Fig. 7, as well as for silver-base and gold-base solid solutions, Figs. 8 and 9. Furthermore, all data available on solid-solution additions to other metals, such as aluminum, magnesium, zinc, platinum, palladium, tin, lead, molybdenum, and tungsten, indicate that this linear relationship is a fundamental property of solid-solution conductors.

It appears justified, therefore, to draw a conductivity vs. temperature coefficient of resistance curve for the various solvent metals, such as shown in Fig. 10. The slope,  $\beta$ , of each of these straight lines gives a constant which is a characteristic of the solvent metal, as indicated in Table I.

The capacity of each metal to form solid solutions with other metals, and their specific influence on the

Table I. Electrical Constants of Metals

| Metal     | Pure Metal Constants                |                      | Solvent Metal Constant<br>$\beta$ value,<br>°C per microhm-cm |
|-----------|-------------------------------------|----------------------|---------------------------------------------------------------|
|           | $\kappa$ , Reciprocal<br>microhm-cm | $\alpha$ ,<br>per °C |                                                               |
| Silver    | 0.629                               | 0.00410              | 153                                                           |
| Copper    | 0.5896                              | 0.00392              | 150                                                           |
| Gold      | 0.4502                              | 0.00394              | 114                                                           |
| Aluminum  | 0.3766                              | 0.00429              | 87.8                                                          |
| Magnesium | 0.2243                              | 0.0042               | 53.5                                                          |
| Zinc      | 0.169                               | 0.00419              | 40.3                                                          |
| Platinum  | 0.0943                              | 0.00393              | 24.0                                                          |
| Nickel    | 0.1462                              | 0.0069               | 21.2                                                          |
| Tin       | 0.0870                              | 0.00447              | 19.5                                                          |
| Iron      | 0.1030                              | 0.00651              | 15.8                                                          |
| Lead      | 0.0484                              | 0.004                | 12                                                            |

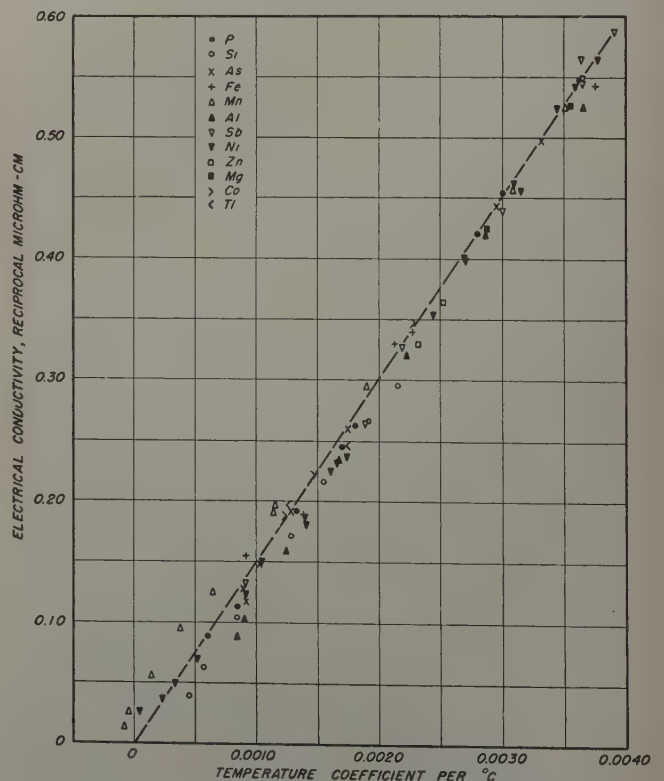


Fig. 6—Electrical conductivity vs. temperature coefficient of resistance of binary copper-base solid solutions.



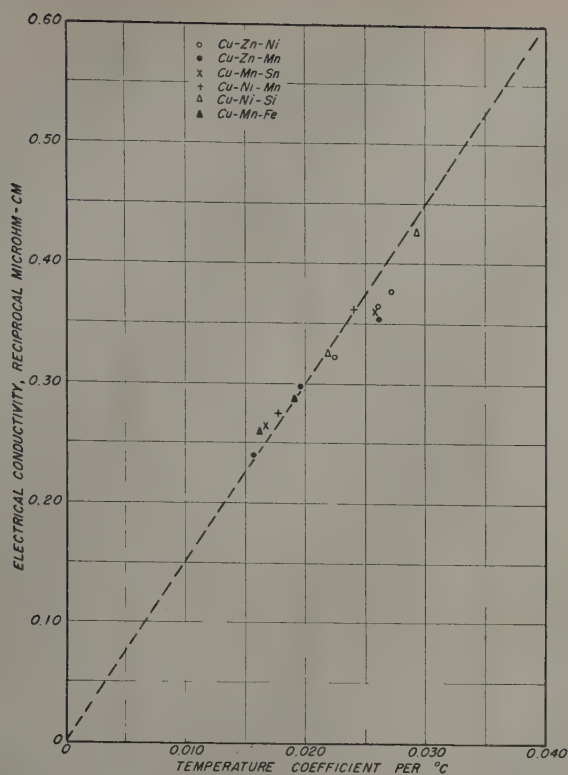


Fig. 7—Electrical conductivity vs. temperature coefficient of resistance of ternary copper-base solid solutions.

electrical properties of the base metal determine how far the straight line for the respective binary, ternary, or more complex solid solutions extends from the point representing the pure solvent metal toward the point of origin of the diagram. The linear plots of Fig. 10 should be considered for approximate purposes only, especially in the low conductivity-low temperature coefficient range, as slight deviations occur for certain solute metals as indicated by Fig. 6. A slight deviation will also occur in solid solutions which undergo a magnetic transformation, as shown for the nickel-rich Cu-Ni solid solutions, Fig. 5.

The existence of the linear correlation between electrical conductivity and temperature coefficient of resistance of solid-solution alloys provides a simple means to predict, within certain limits, temperature coefficients of any single-phase alloy if the conductivity is known, and vice versa. Or if it is desired to achieve a certain electrical conductivity and corresponding temperature coefficient in a given base metal, a large number of alloying components may be used. For example, to achieve 60 pct of the conductivity of standard copper, and its corresponding temperature coefficient of 0.0023 per °C,

Table II. Composition of Copper-Base and Silver-Base Solid Solutions Having Conductivities of 60 Pct I.A.C.S. and Temperature Coefficients of 0.0023 and 0.0021 per °C, Respectively

| Copper-Base Alloys,<br>Wt Pct | Silver-Base Alloys,<br>Wt Pct |
|-------------------------------|-------------------------------|
| 0.075 P                       | 0.12 As                       |
| 0.14 Si                       | (0.2 Al)                      |
| 0.15 Fe                       | 0.21 Sb                       |
| 0.20 As                       | 0.33 Sn                       |
| 0.33 Mn                       | 0.35 Bi                       |
| 0.39 Al                       | (0.4 Ag)                      |
| 0.42 Sb                       | 0.53 Pb                       |
| 0.80 Sn                       | 0.55 Mg                       |
| 0.90 Ni                       | 1.33 Zn                       |
|                               | 4.0 Cd                        |

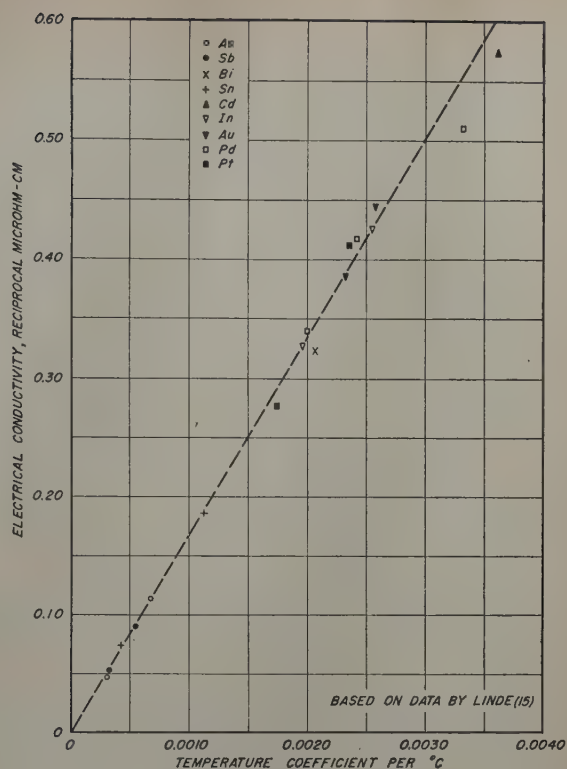


Fig. 8—Electrical conductivity vs. temperature coefficient of resistance of binary silver-base solid solutions.

the various elements listed in Table II can be added to copper in the percentages indicated. Or to obtain the same conductivity, and the corresponding temperature coefficient of 0.0021 per °C for a silver-base alloy, various elements in the percentages also given in Table II may be added to silver.

### Linear Relationship in Binary Systems

For binary systems with a continuous series of solid solutions, two straight lines are found when the conductivity is plotted against the temperature coefficient. Fig. 11 shows such diagrams for the systems

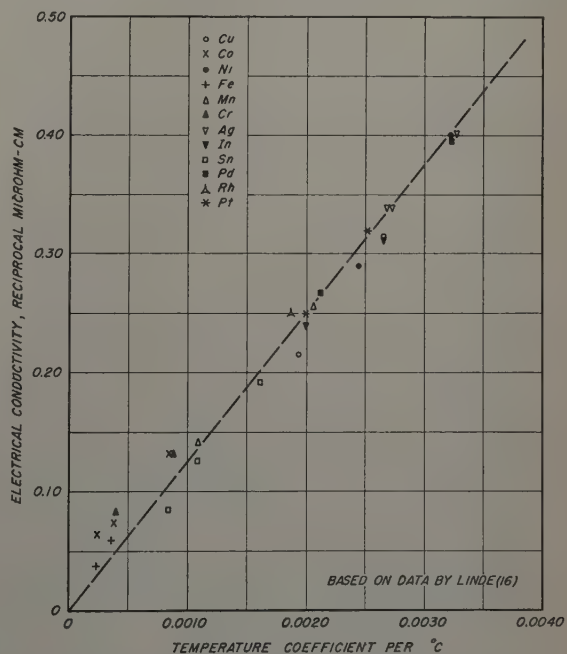


Fig. 9—Electrical conductivity vs. temperature coefficient of resistance of binary gold-base solid solutions.

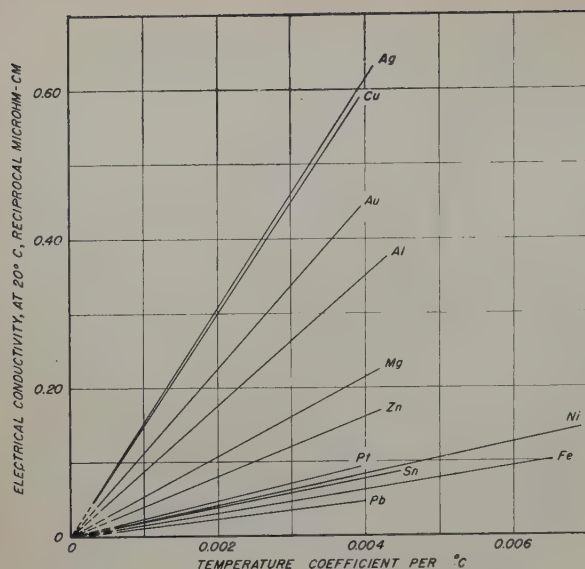


Fig. 10—Electrical conductivity vs. temperature coefficient of resistance of solid solution alloys with various elements as base metals.

Ag-Pd, Au-Pd, and Pd-Pt, based on the data given by Geibel.<sup>17-19</sup> The two branches of the Ag-Pd and Au-Pd alloys represent the conductivity vs. temperature coefficient plot of the silver-rich and gold-rich solid solutions, on one hand, and the palladium-rich solid solutions, on the other. The point of intersection represents—considering possible experimental errors—approximately 50 atomic pct; the actual atomic percentage of palladium of the alloys is indicated beside each point on the diagram. The lines representing the silver-rich and gold-rich solid solutions intersect very close to the origin, whereas the extrapolation of the line representing the palladium-rich solid solutions cuts the abscissa to the left of this point. This may be related to the fact that palladium is a transition metal. Both branches of the conductivity vs. temperature coefficient plot of Pd-Pt solid solutions practically coincide, since the conductivity and temperature coefficient of pure palladium and platinum are almost identical. Again, the lowest point of the plot is about 50 atomic pct.

For binary alloy systems in which the component metals are soluble in each other to a limited extent and do not form an intermediate phase, the conductivity-temperature coefficient diagram consists of

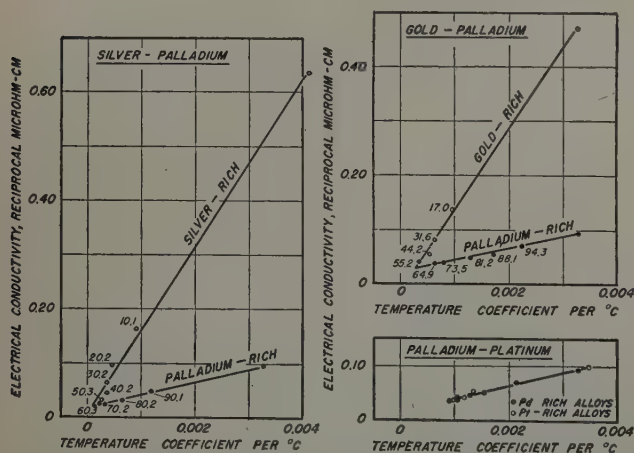


Fig. 11—Electrical conductivity vs. temperature coefficient of resistance diagrams of the systems Ag-Pd, Au-Pd, and Pd-Pt.

two straight lines representing the electrical properties of the primary solid solutions and a third straight line joining the points representing the saturated solid solutions for each phase. This is illustrated in Fig. 12 by data for the Cu-Co<sup>20</sup> and Cu-Ag<sup>21</sup> systems.

### Norbury and Kuwada Relationship

Norbury and Kuwada<sup>5</sup> tried to find a correlation between electrical resistivity and temperature coefficient of resistance of copper-base alloys. The temperature coefficient they used was defined as  $\alpha' = \frac{\Delta R}{\Delta t}$ , rather than as  $\alpha = \frac{\Delta R}{\Delta t R_0}$ , which is normally used. On the basis of resistivity measurements of copper alloys containing aluminum (up to 3.8 pct), tin (up to 3.9 pct), and silicon (up to 2.7 pct) at various temperatures between  $-191^\circ$  and  $438^\circ\text{C}$ , they claimed that a linear relationship between resistivity at  $0^\circ\text{C}$  and  $\alpha' = \frac{\Delta R}{\Delta t}$  (for that temperature range) exists, which may be expressed by the equation:

$$\alpha' = (0.0064 + R_0 \times 0.0002) \text{ microhms-cm per } ^\circ\text{C} \quad [1]$$

Their data are shown in Fig. 13, together with those of some Cu-Ni and Cu-Mn solid solutions. The values for the latter do not follow the linear correlation, as their resistivity does not change linearly between  $-191^\circ$  and  $438^\circ\text{C}$ .

In order to throw further light on Norbury and Kuwada's relationship, data obtained by other authors have been similarly evaluated. Fig. 14 shows

resistivity vs.  $\frac{\Delta R}{\Delta t}$  based on data by Smith and Palmer<sup>2</sup>; the  $\frac{\Delta R}{\Delta t}$  values were calculated using re-

sistivity values for  $20^\circ\text{C}$  and  $\alpha = \frac{\Delta R}{\Delta t R_{20^\circ\text{C}}}$  values de-

termined from resistivity data at  $200^\circ$  and  $20^\circ\text{C}$ . It follows from Fig. 14 that the curves for Cu-Si and Cu-Al solid solutions deviate substantially from each other, and do not obey the relationship of eq 1. The solid solutions with the transition elements manganese and nickel behave very differently; with

relatively low nickel contents, the  $\frac{\Delta R}{\Delta t}$  values are

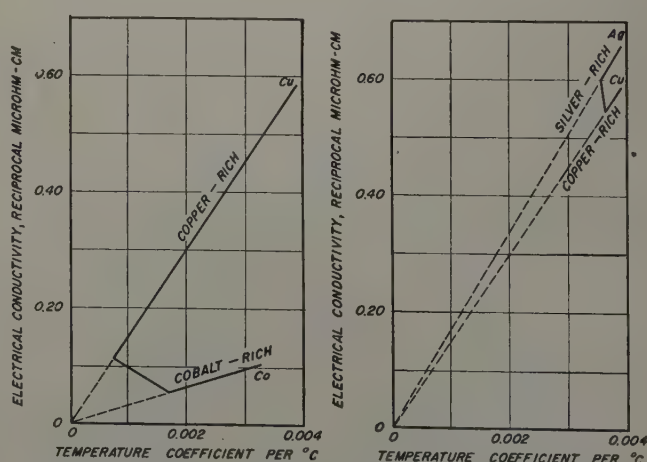


Fig. 12—Electrical conductivity vs. temperature coefficient of resistance diagrams of the systems Cu-Co and Cu-Ag.



somewhat larger, and above 20 pct Ni they become smaller, than that of pure copper.

In a similar way, data given by Linde<sup>7</sup> have been evaluated; the  $\frac{\Delta R}{\Delta t}$  values were based on resistivities at  $-183^\circ$  and  $0^\circ\text{C}$ . The results for the solid solutions with arsenic and antimony did not obey Norbury and Kuwada's relationship. Again, the alloys with manganese, and also with iron, behave quite differently, although their temperature coefficient of resistance is constant between  $-183^\circ\text{C}$  and room temperature.

In general, it can be said that eq 1 does not hold for all copper-base solid solutions, even if the transition elements are excluded as solvents. Hence, this relationship cannot be regarded as a means of predicting resistivity of copper-rich solid solutions if  $\frac{\Delta R}{\Delta t}$  is known, and vice versa. On the other hand, the linear relationship between electrical conductivity and the temperature coefficient of  $\alpha = \frac{\Delta R}{\Delta t R_0}$  essentially holds for all solid-solution alloys, regardless of the base metal.

### Conclusions

1—A linear relationship has been found to exist between the electrical conductivity and temperature coefficient of resistance ( $\alpha = \frac{\Delta R}{\Delta t R_0}$ ) for all solid-solution components added to a given metal solvent.

2—Each solvent metal has its own distinctive  $\beta$  value—defined as the slope of the electrical conductivity-temperature coefficient of resistance plot.

3—Of the common metals, the  $\beta$  value is highest for silver, and progressively smaller for copper, gold, aluminum, magnesium, zinc, platinum, nickel, tin, iron, and lead.

4—Knowledge of this relationship permits quick approximation of the temperature coefficient of resistance of a solid-solution alloy by measurement of its conductivity, or vice versa.

### Acknowledgments

The authors wish to thank the U. S. Signal Corps Engineering Laboratories, Fort Monmouth, N. J., for

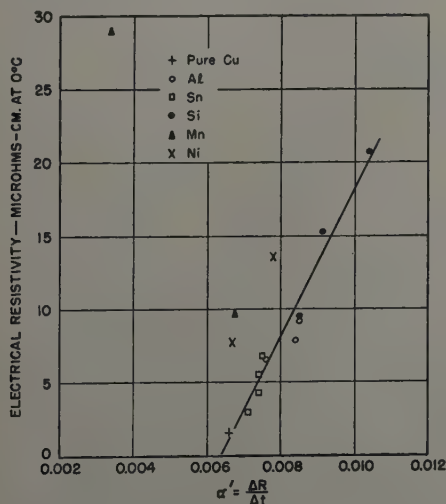


Fig. 13—Values of  $\frac{\Delta R}{\Delta t}$  vs. resistivity at  $0^\circ\text{C}$  of solid solutions of copper with various elements (based on data by Norbury and Kuwada).

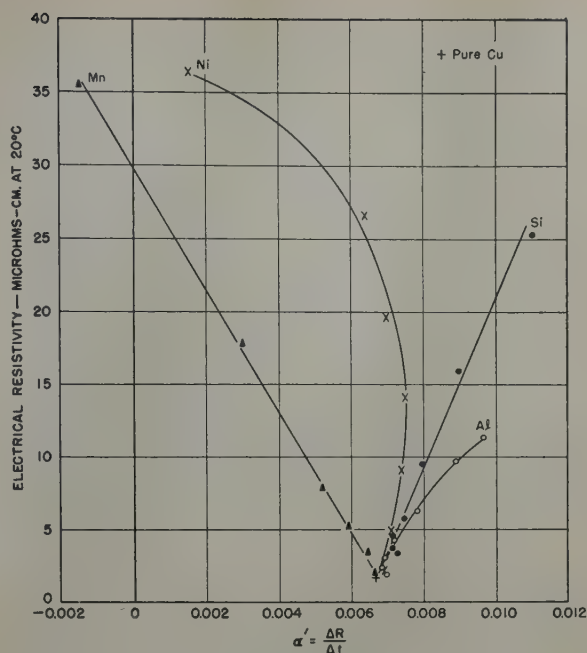


Fig. 14—Values of  $\frac{\Delta R}{\Delta t}$  vs. resistivity at  $20^\circ\text{C}$  of solid solutions of copper with various elements (based on data by Smith and Palmer).

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# Metallurgical Mechanism for Mercury Stress Cracking Of Copper Alloys

by W. D. Robertson

SINCE the comprehensive paper of Moore, Beckinsale, and Mallinson,<sup>1</sup> little consideration has been given to the mechanism of mercury stress cracking of copper-base alloys, apart from extensive work on metallurgical and fabrication variables employing mercurous nitrate as an evaluation test. However, with the phase diagrams now available and the recent considerations of interfacial tension at grain boundaries, developed by Smith,<sup>2</sup> it appears that the elements of a detailed solution to the problem are available.

The facts that require explanation are:

1—Pure copper is not embrittled by mercury, with or without an applied or residual stress.

2—Cu-Zn and other copper-base alloys, in excess of some undefined solute concentration, are embrittled provided an external or residual stress is acting; cracking is not observed in the absence of stress.

3—The path of fracture is invariably intergranular.

4—Copper and copper-base alloys do not dissolve readily in mercury at room temperature.<sup>1</sup>

Consideration of the Cu-Hg phase diagram<sup>3</sup> shows that, at room temperature, solution of copper in mercury is probably limited by the formation on the surface of a microscopically thin layer of intermetallic compound, CuHg, having a very limited range of solubility which effectively restricts diffusion of copper and mercury. But, above 150°C (the highest peritectic temperature) copper solid solution is in equilibrium with a liquid Hg-Cu solution and, consequently, copper should dissolve freely in a large volume of mercury with the formation of an equilibrium dihedral angle at grain boundaries in contact with the liquid phase. Depending on the magnitude of this angle, mercury will or will not penetrate the solid phase along grain boundaries and spread over grain faces. Thus the measurement of the dihedral angle of grain boundaries in equilibrium with the liquid phase above 150°C should indicate whether copper is intrinsically resistant to embrittlement by mercury. In view of the fact that mercury is appreciably soluble in copper, it may also be anticipated that diffusion of mercury will take place at higher temperatures in the absence of the intermetallic compound and possibly at a more rapid rate along grain boundaries than through the grains, resulting in a Cu-Hg alloy of unknown properties.

In the case of brass, the ternary system Cu-Zn-Hg is involved and, from the resistance of brass to general solution in mercury at room temperature, it is probable that a compound of limited solubility range also exists, similar to the binary Cu-Hg sys-



Fig. 1—Copper annealed at 700°C, immersed in mercury at 170°C. X300.

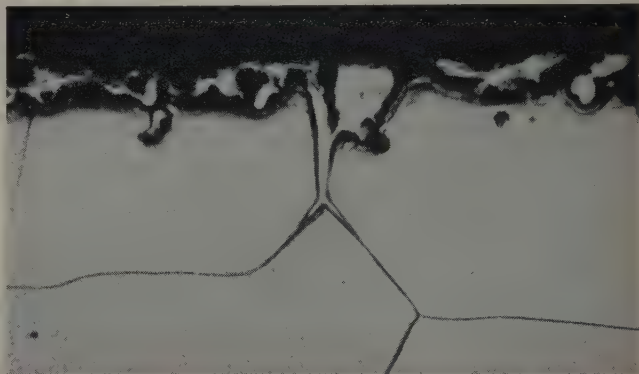


Fig. 2—Brass (69 pct Cu) annealed at 850°C, immersed unstressed in mercury at 350°C. X150.

tem. Also, compared with copper, a change in the dihedral angle at grain boundaries in contact with mercury may be expected to result from the addition of zinc to copper. The preceding generalizations appear to be confirmed by the following experiments.

## Experimental Results

Oxygen-free copper wire, annealed at 700°C for 3 hr in copper foil, was immersed in mercury at 170°C, with and without an applied stress. After 24 hr immersion, specimens which were spring loaded to a nominal stress of 10,000 psi had not failed, and there was no apparent embrittlement as indicated by a 180° bend around a diameter approximately equal to the diameter of the wire (0.125 in.): General solution of the surface had taken place, indicated by a change in diameter of the wire, and the resulting structure of the surface is shown in Fig. 1. It is apparent that angles have developed at grain boundaries and examination at a high magnification indicates that the angle is in excess of 120°, completely excluding penetration of mercury. In view of the measurements made by Smith<sup>2</sup> on the

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Cu-Pb system, it may be assumed that the dihedral angle does not vary greatly with temperature and, therefore, the value obtained at 170°C is applicable at room temperature. It may also be assumed that the applied stress will not appreciably affect the angle, and examination of both stressed and unstressed specimens indicates that the apparent angles are similar in both cases which is, in part, confirmed by the fact that none of the stressed specimens failed.

Brass sheet (69 pct Cu), after annealing at 850°C for 3 hr followed by slow cooling, was immersed, unstressed, in mercury at 170°C for 40 hr. A 90° bend at room temperature, after evaporation of the mercury at a low pressure, showed embrittlement at grain boundaries, but angles were not well developed and there was no significant general solution of the alloy. Consideration of the possible ternary system now involved indicated that a higher temperature might be required, and a second test was conducted, unstressed, at 350°C for 18 hr. Complete embrittlement resulted together with general solution of the brass. The microstructure, Fig. 2, reveals the cause of embrittlement. It is apparent that a layer of a second phase has formed, probably on cooling to room temperature, and the dihedral angle has changed from the large value characteristic of copper to something much less than 60° as a result of the addition of zinc to the alloy. Instead of the alloy dissolving in mercury with the formation of a large dihedral angle, extensive penetration of the grain boundaries by the phase present on the surface has taken place.

These experiments apparently lead to the following conclusions regarding the mechanism of stress cracking of copper-base alloys in mercury.

1—Copper is not susceptible to mercury cracking because the equilibrium dihedral angle formed at grain boundaries in contact with mercury is such that penetration is impossible.

2—Cu-Zn alloys, above some zinc concentration to be determined by quantitative measurement of the angles as a function of zinc concentration, may be embrittled by mercury because the dihedral angle formed by the solid solution and liquid mercury is less than 60° leading to penetration under equilibrium conditions and in the absence of an applied or residual stress.

3—At room temperature, equilibrium between brass and liquid mercury is not attained owing to the formation of an intermetallic compound which prevents continued penetration. If, however, an external or residual stress is present, the brittle compound formed at the surface is fractured allowing further contact of the alloy with mercury and continued penetration in accordance with the small dihedral angle.

Fig. 3 shows the initial stage in the fracturing of the brittle phase by bending the brass sheet after cooling to room temperature and evaporating mercury at a low pressure. Fig. 4 shows that a grain, which was surrounded at the higher temperature in the absence of stress, can be completely separated from the matrix by bending at room temperature. It is apparent that the path of fracture is through the brittle phase formed in the grain boundaries.

Thus the function of stress is apparently defined as a mechanical aid to the continued contact of the alloy with mercury. Basically, the problem is resolved in terms of the equilibrium dihedral angle. The limiting zinc concentration above which Cu-Zn alloys may be embrittled by mercury is, to a first

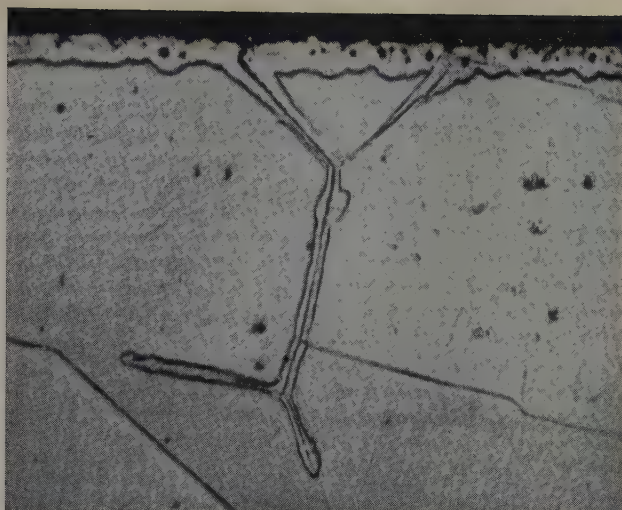


Fig. 3—Brass (69 pct Cu) annealed at 850°C, immersed unstressed in mercury at 350°C, and bent at room temperature after evaporation of mercury at a low pressure. Initial stage of fracture passing through brittle phase at grain boundaries.



Fig. 4—Brass (69 pct Cu) annealed at 850°C, immersed in mercury at 350°C, and bent at room temperature after removal of mercury by evaporation at a low pressure. Final stage of fracture passing through brittle phase at grain boundaries.

approximation, defined by the alloy in which the dihedral angle is less than 60°; measurements are now being made to determine quantitatively the equilibrium angle as a function of zinc concentration and temperature.

Mercury stress cracking appears, therefore, as a problem in interfacial tension and intermetallic compounds, and no special properties of grain boundaries need be invoked, other than interfacial energy relationships and their dependence on alloying and orientation.

### Acknowledgment

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# Rate of Evaporation of Zinc at Low Pressures

by H. W. St. Clair and M. J. Spendlove

**An automatic surface-follower mechanism was used to measure the surface temperature and the rate of evaporation of molten zinc while undergoing distillation at low pressure. At pressures of 50 to 100 microns Hg, the rate of evaporation may be 60 to 80 pct of the theoretical maximum corresponding to the measured temperature. The rate decreases rapidly at pressures above 100 microns Hg, to only 7 pct of the theoretical maximum at 2000 microns Hg. Measured temperature gradients at the surface are in agreement with theoretical gradients calculated from the heat of vaporization, rate of evaporation, and thermal conductivity of molten zinc.**

**T**HIS paper covers a series of careful measurements of the rate of evaporation of molten zinc at low pressures, undertaken as a part of a general investigation on the separation of metals by distillation.<sup>1</sup> Preliminary results on the rate of evaporation of zinc were described in a previous publication.<sup>2</sup> The results of the preliminary study are as follows:

1—The observed rates of evaporation of zinc were as high as 0.60 g per sq cm per min, corresponding to 75 pct of the maximum rate as determined by the temperature of the metal.

2—The evaporation rate was decreased from 0.30 g per sq cm per min at a pressure of 25 microns to only 0.09 g per sq cm per min when the pressure was increased to 5 mm.

3—The temperature of the surface during rapid evaporation may be 35° to 100°C less than the main mass of metal. Observed temperature gradients at the surface are consistent with those calculated from the heat of vaporization and the thermal conductivity of liquid zinc.

In the preliminary experiments, the rate of evaporation was determined from the loss in weight of the metal in the crucible during the test. This was compared with the weight of the condensate. Obviously, this method was subject to error because of some

uncertainty as to the period of evaporation that should correspond to the loss in weight. Furthermore, this method did not permit taking into account probable variations in the rate of evaporation during the test. A more serious shortcoming was that the temperature at the evaporating surface was not known, so the maximum theoretical rate of evaporation could not be calculated accurately.

To improve the precision of rate measurements and to allow accurate measurements of the surface temperature, a refined experimental technique was developed whereby the temperature and position of the surface could be measured accurately. This was done by an automatic surface-follower mechanism that gave a continuous record of the surface temperature and the amount of zinc evaporated. These data permitted an instantaneous determination of the actual rate of evaporation and the surface temperature throughout the test. Pure zinc (99.99 pct Zn) was used in all experiments.

## Description of Distillation Furnace

The details of construction of the distillation furnace are shown in Fig. 1. The furnace is enclosed in a large quartz tube open at one end. The open end of the quartz tube is sealed by means of a water-cooled head. The entire enclosure is vacuum tight. The connection between the water-cooled head and the quartz tube is sealed by means of a rubber gasket which fits tightly against the smooth end of the tube. The metal is heated by induced current set up in the molten zinc and the walls of the graphite crucible by means of a water-cooled induction coil outside the quartz tube. High frequency current is passed through the induction coil from a 6 kw mer-

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cury-spark-gap frequency converter. The enclosure is evacuated by means of a rotary vacuum pump connected to the water-cooled head by a 2 in. pipeline. The condenser projects inside the quartz tube and is supported above the crucible by two cooling-water tubes that connect the condenser cooling coil to the condenser flange. The condenser insert sleeve extends from the condenser into the annular groove in the top of the crucible wall to prevent the escape of zinc vapor from between the crucible and the condenser. The flange on the condenser assembly fits tightly against the flange section at the upper end of the head. Coupling between the two flanges is likewise sealed by a rubber gasket. The atmospheric pressure acting against the flanges is sufficient to insure a vacuum-tight system.

The temperature of the main mass of metal in the crucible is measured by a thermocouple that projects up through the rubber stopper at the bottom of the quartz tube into a thermocouple well in a re-entrant dome at the bottom of the graphite crucible. Thermocouple wires in the base of the crucible are electrically shielded by the graphite crucible and the metal it contains. The surface-follower thermocouple wires are shielded by the water-cooled condenser. The absence of induction heating in the thermocouple wires was verified by measuring the melting point of zinc with power on the induction furnace and then observing the same temperature for the freezing point with the power turned off.

Pressure within the enclosure is measured by an ionization vacuum gage. A McLeod gage is used to verify all pressure-reading instruments at frequent intervals.

The zinc vapors evaporating from the surface of the molten metal rise to the water-cooled condenser, where they are collected on the cylindrical iron insert sleeves, which are removed from the condenser when the condensate is to be stripped.

### Operation of the Follower Unit

To measure the surface temperature of the metal during the course of an evaporation experiment, a special surface-follower mechanism was designed. It is schematically illustrated in Fig. 2. The surface-follower mechanism is mounted on a base plate that fits against the water-cooled condensing head (6) shown in Fig. 1. The surface-follower electrode (16) is supported by a movable carriage (7). The carriage is raised and lowered by means of a pair of vertical screws driven by a dc motor through a reduction gear. The motor runs continuously and is coupled to the carriage mechanism by means of a magnetic clutch (3). The clutch is energized through a set of contacts on a low-voltage relay. At the instant the follower electrode touches the metal surface, the relay circuit is closed and contacts for the magnetic clutch are opened. The de-energized clutch then slips, and the downward motion of the carriage stops, leaving the electrode and the thermocouple exactly at the metal surface. The downward motion starts again when the surface of the metal is lowered sufficiently by evaporation so that electrical contact with the surface-follower electrode is broken. This mechanism permits the follower electrode to indicate the rate of evaporation of the metal very accurately. During an evaporation test, the magnetic clutch engages and disengages with great rapidity.

A thermocouple for measuring the surface temperature is mounted on the same carriage as the surface-follower electrode. The position of this

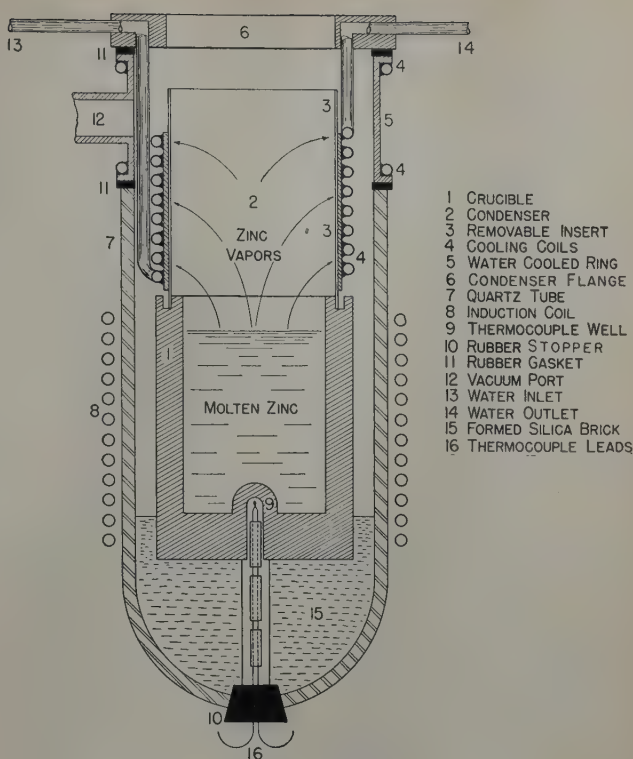


Fig. 1—Vacuum distillation unit.

thermocouple is adjusted carefully at the beginning of the test by means of the thumb screw (9). The wall thickness of the protection tube is made very thin at the closed end where the thermocouple junction is located. The temperature indicated by the thermocouple is quite sensitive to the relative position of the thermocouple tube. The indicated temperature increases as the thermocouple is immersed below the surface and decreases above the surface, but there is a marked discontinuity in the temperature gradient at the surface. This discontinuity serves to indicate the proper position for the thermocouple to give an accurate indication of the surface temperature. It was found that the tube was in

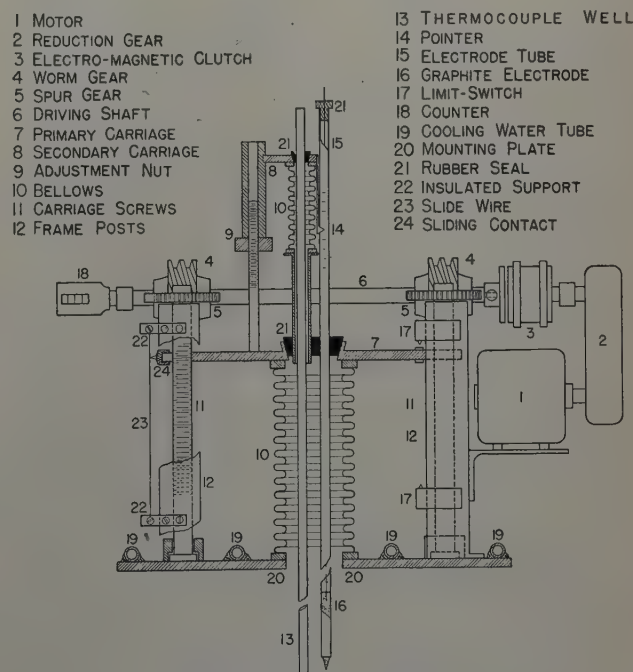


Fig. 2—Surface-follower unit.

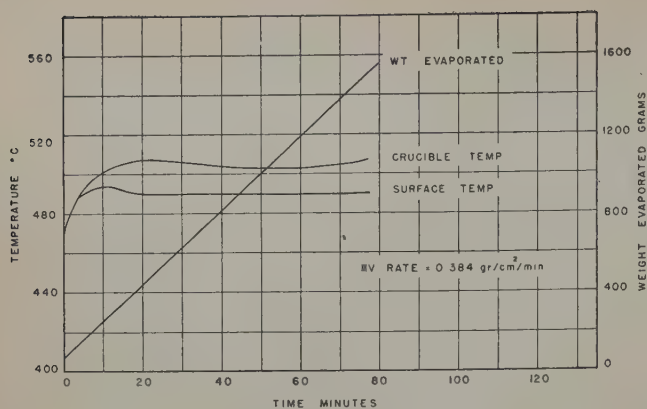


Fig. 3—Typical distillation test.

proper position when the tip of the protection tube projected approximately 1 mm into the liquid metal. Preliminary sensitivity tests revealed that the probable maximum departure from this position is 0.019 cm. The thermocouple response to such a variation in depth of immersion is negligible.

Movement of the carriage is permitted by sylphon bellows soldered to the carriage and base plate. Another smaller bellows is provided for the thermocouple support. The thumb screw and small bellows permit movement of the surface thermocouple to determine the variation of temperature above and below the evaporating surface during a test.

The position of the follower electrode is indicated by a counter attached to the shaft of the screw mechanism. The position is also recorded automatically by means of a sliding contact (24) upon the carriage, which picks up a voltage from the potentiometer (23). A constant low voltage is applied to the ends of the wire (22). The potential of the sliding contact is linearly related to the distance the carriage is above the zero position. This voltage is recorded on the strip-chart potentiometer and is easily calibrated to read in terms of weight of metal evaporated. The slope of the voltage-time curve is therefore proportional to the rate of evaporation. More accurate determination of the surface displacement is obtained by the revolution counter on the main drive shaft. The automatic surface follower thereby provides a means for simultaneously determining the surface temperature and the rate of evaporation at any time during the test.

A complete description of the mechanical and electrical characteristics is beyond the scope of this paper, but a detailed discussion of these is presented elsewhere.<sup>3</sup>

### Experimental Procedure

The general procedure followed in most of the evaporation tests was to evacuate the system to a pressure of the order of 25 microns and then raise the metal temperature to start evaporation. Evaporation begins shortly after the temperature exceeds the melting point. The follower electrode was lowered to the metal surface after the metal was completely melted but before appreciable evaporation had occurred. It was necessary to keep the electrode above the surface until after the metal was melted to avoid breaking the electrode tip on the solid metal when the electrode made contact.

In some experiments the metal was heated before evacuation. Evaporation was started by suddenly reducing the pressure in the system. In this way it

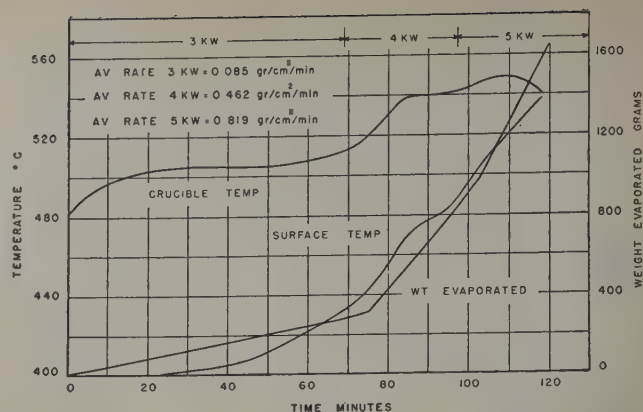


Fig. 4—Typical test on the distillation of zinc at different rates of evaporation.

was possible to obtain better control over the exact time at which evaporation started, but precautions had to be taken because of the sudden release of absorbed gas. The rapid evolution of the gas from the metal sometimes caused droplets of the metal to become entrained in the out-rushing gas and thereby were carried to the condenser by mechanical means rather than by true evaporation. Although the metal surface could not be observed visually in these experiments, the condition was determined by supplemental tests. A window section was put in the place of the follower unit and the metal surface was visually observed throughout the distillation period. Details of these observations are reported in another paper.<sup>2</sup> Early in the evaporating period a heavy film of fine material collects over most of the surface and then gradually disappears as the system comes up to temperature. The surface remains clean for the remainder of the test. Only slight turbulence of the zinc bath could be noted. The same conditions are assumed for experiments with the automatic surface follower.

### Results of Distillation Experiments

The results of a typical distillation test are shown in Fig. 3, in which the weight of metal evaporated, the crucible temperature, and the temperature of the surface of the metal are represented graphically against the duration of the test. It will be observed that there is a fairly constant rate of evaporation even at the beginning of the test when the temperature has not quite risen to maximum. The crucible temperature rises sharply to about 500°C, after which it levels off and becomes fairly constant. The surface temperature is about 15° to 20° lower than the crucible temperature.

During this test, the loss in weight of the crucible amounted to 1542 g, as compared to 1523 g, the weight of the condensate collected in the condenser. The weight of zinc indicated by the counter on the surface-follower mechanism was 1544 g, which agreed very well with the loss in weight of the crucible. The average rate of evaporation for the entire test per unit area of surface of the metal exposed to low pressure amounted to 0.384 g per sq cm per min. These data are typical. The weight of zinc evaporated as indicated by the counter usually approximates very accurately the loss in weight of the crucible. Weight of the condensate is usually about 10 to 20 g less than the weight of metal evaporated. This small amount of zinc vapor is lost by diffusion to other parts of the evacuated enclosure.

In test 24, Fig. 4, evaporation was started at a



power input of 3 kw. During this time the rate of evaporation was fairly constant, even though the crucible temperature was rising at the beginning and near the end of this part of the test. After about 70 min, power was increased to 4 kw. Shortly afterward, the rate of evaporation increased rather abruptly. The crucible temperature likewise increased and leveled off at 540°C. After 30 min, the power was increased further to 5 kw, and again the rate of evaporation increased proportionally. Tests shown in Figs. 3 and 4 were made at a pressure of 15 to 20 microns.

The interesting fact brought out by this experiment is that the rate of evaporation is more definitely related to the power input than to the crucible temperature or the surface temperature as recorded by the thermocouple on the surface follower. The surface temperature, as shown in this experiment, is abnormally low throughout most of the test, and it is likely that it does not represent the average surface temperature.

### Theory of Rate of Evaporation

The principal advantage of evaporation at reduced pressure is that high rates of evaporation are attained at relatively low temperatures. Evaporation at atmospheric pressure is retarded because the preponderance of gas molecules above the evaporating metal greatly impedes the diffusion of vapor molecules away from the surface. Under equilibrium conditions, such as exist when vapor-pressure measurements are made, the rate of evaporation from the molten metal is equal to the rate of condensation back onto the evaporating surface. The following expression has been derived from the effusion formula to express the theoretical maximum rate of evaporation into a perfect vacuum:<sup>2</sup>

$$W_o = p_o \alpha \sqrt{\frac{M}{2RT}} \quad [1]$$

where  $M$  is the molecular weight;  $R$ , the gas constant;  $p_o$ , the vapor pressure at temperature  $T$ ; and  $\alpha$ , the coefficient of condensation. As the value of  $\alpha$  is virtually unity for metals, the maximum rate of evaporation of zinc can be given by:

$$W_o = \frac{28.30 p_o}{T^{1/2}} \quad [2]$$

in which  $W_o$  is expressed in g per sq cm per min. This equation has been used to calculate the maximum rate of evaporation as given in this paper.

At very low pressures, the vapor molecules themselves offer the only impediment to the diffusion of vapor away from the surface. Their presence above the evaporating surface causes many molecular collisions, which cause some condensation back onto the surface. There is, however, a net rate of evaporation and recondensation. If, under these conditions, the partial pressure of the zinc vapor is  $p$ , the net rate of evaporation will be:

$$W = W_o \frac{28.30 p}{T^{1/2}} \quad [3]$$

which, combined with eq 2, gives:

$$W = \frac{28.30}{T^{1/2}} (p_o - p) \quad [4]$$

Table I. Rate of Evaporation of Zinc at Various Pressures. Power 3.5 kw

| Test No. | Pressure, Microns | Avg Surface Temperature, °C | Rates: G per Sq Cm per Min |              | $\frac{W}{W_o}$ | Vapor Saturation,* $\frac{p}{p_o}$ |
|----------|-------------------|-----------------------------|----------------------------|--------------|-----------------|------------------------------------|
|          |                   |                             | Max. $W_o$                 | Observed $W$ |                 |                                    |
| 1a       | 100               | 489                         | 1.05                       | 0.625        | 0.596           | 0.404                              |
| 1b       | 300               | 496                         | 1.24                       | 0.625        | 0.504           | 0.496                              |
| 1c       | 800               | 511                         | 1.80                       | 0.417        | 0.232           | 0.768                              |
| 2a       | 100               | 484                         | 0.93                       | 0.768        | 0.826           | 0.174                              |
| 2b       | 300               | 497                         | 1.27                       | 0.645        | 0.508           | 0.492                              |
| 3a       | 1500              | 513                         | 1.90                       | 0.272        | 0.143           | 0.857                              |
| 4a       | 500               | 498                         | 1.27                       | 0.385        | 0.303           | 0.697                              |
| 4b       | 1000              | 524                         | 2.45                       | 0.253        | 0.104           | 0.896                              |
| 4c       | 1500              | 537                         | 3.45                       | 0.123        | 0.036           | 0.964                              |
| 5a       | 1000              | 457                         | 0.46                       | 0.336        | 0.730           | 0.260                              |
| 5b       | 1500              | 511                         | 1.80                       | 0.320        | 0.178           | 0.822                              |
| 5c       | 2000              | 525                         | 2.50                       | 0.177        | 0.071           | 0.929                              |
| 6a       | 50                | 457                         | 0.46                       | 0.647        |                 |                                    |
| 6b       | 100               | 485                         | 0.95                       | 0.647        | 0.680           | 0.320                              |
| 6c       | 500               | 485                         | 0.95                       | 0.444        | 0.468           | 0.532                              |
| 6d       | 1000              | 487                         | 1.00                       | 0.251        | 0.251           | 0.749                              |

\* Vapor pressure of zinc for this calculation from U. S. Bureau of Mines, Bull. 383, p. 109.

As the observed rate of evaporation is  $W$  at a temperature for which the maximum rate of evaporation is  $W_o$ , it may be concluded that the zinc vapor is partly saturated. The degree of saturation represented by  $p/p_o$  is equal to:

$$p/p_o = 1 - W/W_o \quad [5]$$

### Variation of Evaporation Rate with Residual Gas Pressure

The rate of evaporation was measured for several tests in which the residual gas pressure was regulated at various assigned values while the power was held constant at 3.5 kw. The results of the tests are summarized in Table I. Variation of the observed rate of evaporation with respect to residual gas pressure is illustrated graphically by the solid line in Fig. 5. The rate of evaporation falls rapidly as the pressure is increased. A similar trend is shown by data obtained in previous experiments at lower rates of evaporation. These data are represented by the two dotted lines, representing evaporation at 1.9 and 1.2 kw, respectively.

The regulation of pressure at pressures of 100 microns or below was difficult because of the greater

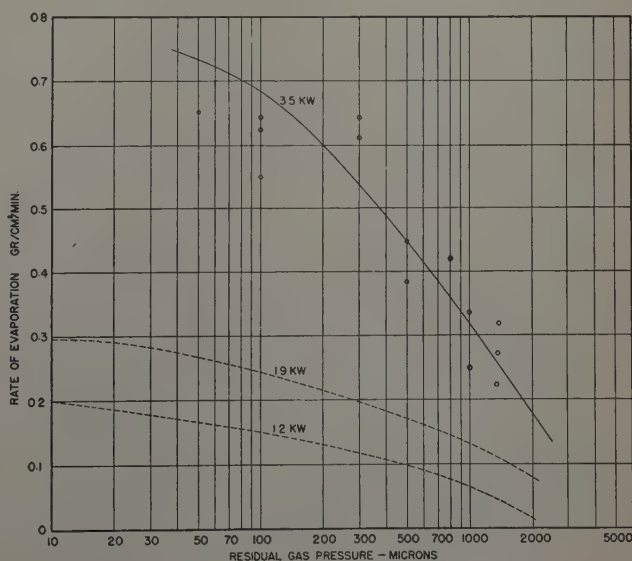


Fig. 5—Rate of evaporation vs. residual gas pressure.

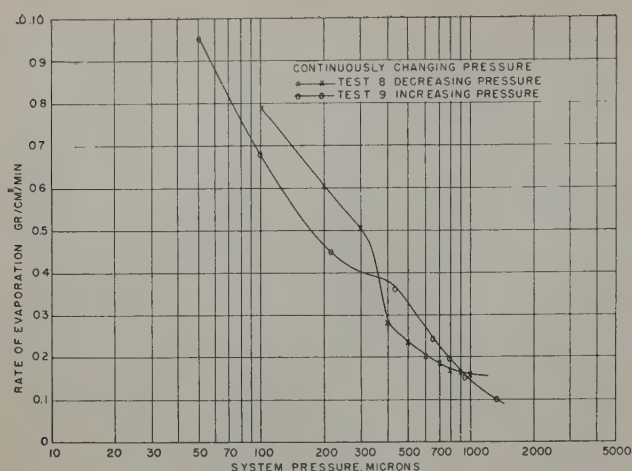


Fig. 6—Rate of evaporation in relation to continuously changing residual gas pressure.

time required for the vacuum pump to reduce the pressure, if it should momentarily be allowed to become too high. Therefore, no attempt was made to regulate the pressure below 100 microns. However, the rate of evaporation at 50 to 100 microns is of the order of 60 to 80 pct of the maximum rate, so that reducing the residual gas pressure below 100 microns will have much less effect than a corresponding decrease at higher pressures. It should be pointed out that the residual gas pressure as measured by the vacuum gage does not represent either the total gas pressure or the partial pressure of the residual gas at the evaporating surface. The partial pressure of the zinc may be many times the residual gas pressure. Furthermore, the partial pressure of the residual gas at the metal surface may be many times less than that in the condenser, because the evaporating zinc vapor sweeps the permanent gas molecules away. In other words, the evaporating zinc vapor has the same effect as mercury vapor in a diffusion pump.

At lower pressures there is greater freedom for effusion of vapors away from the molten metal surface, and the observed rate of evaporation becomes correspondingly nearer the calculated maximum rate as determined from the measured surface temperature. A comparison of the observed and maximum rate of evaporation is given in Table I under the heading  $W/W_0$ . In one instance the observed rate of evaporation is about 83 pct of the maximum at 100 microns. At 2000 microns it is about 7 pct of the maximum. The theoretical maximum rate of evaporation cannot be reached at high rates of evaporation even at extremely low pressures, because the greater concentration of vapor molecules above the surface

will partly obstruct the flow of other vapor molecules from the surface.

The effect of an increase in pressure of the residual gas in the system is to impede the diffusion of molecules of zinc vapor away from the surface, thereby increasing the partial pressure of zinc. The degree of saturation of the zinc vapor at the surface may be calculated from the observed rate of evaporation and the maximum rate corresponding to the surface temperature as shown in eq 5. The saturation as thus determined was as low as 17 pct at 100 microns pressure but increased to 96 pct at 2000 microns.

Two experiments were run in which the rate of evaporation was measured while the residual gas pressure was being continuously increased or decreased. In experiment 8, the pressure was gradually reduced at a uniform rate from 1000 to 100 microns. In experiment 9, the pressure was increased in the same manner at approximately the same rate from 50 to 1500 microns. These pressure adjustments were made by manually manipulating vacuum valves to throttle the vacuum pump. A careful record of the pressure measurements was kept throughout each test. Rates of evaporation corresponding to many different pressure measurements were calculated for each experiment. Two values for the rate of evaporation were thus obtained for each pressure. These data are represented graphically in Fig. 6.

In both experiments, an anomalous change in rate of evaporation occurs at pressures in the range of 300 to 400 microns. There is a sudden rise in the observed rate when the pressure decreases through this range, and the rate becomes more nearly constant when the pressure is increased through this range. No satisfactory explanation for this phenomenon has yet been determined.

The temperature decreased gradually from 489° to 447°C in test 8 and increased from 447° to 482°C in test 9. Temperature variations for the two tests are so nearly identical that curves are omitted for reasons of simplicity.

A series of tests was made to observe the rate of evaporation at several different power levels. These tests were continued for relatively long periods. The results are presented in Table II.

These data show that the total weight of the metal evaporated can be measured rather accurately by the surface-follower mechanism, the greatest error being about 2 pct in test 23. The relation between total power and the rate of evaporation is illustrated graphically in Fig. 7. It shows the total power required to evaporate at the observed rate. The curve is extrapolated to zero rate of evaporation and indicates that about 1.5 kw is needed to hold the system temperature at a point where evaporation starts. The power required for vaporization of zinc at the observed average rate of evaporation also is shown. The difference between the two curves represents the power losses.

It has been stated previously that starting evaporation by suddenly reducing the gas pressure above the molten metal is likely to result in an apparent rate of evaporation that is higher than the true rate would be. This is brought about by the rapid escape of absorbed gas, which carries droplets of metal from the molten surface into the condenser, where it solidifies as though it had actually been evaporated. Only five such tests were considered to give dependable rates of evaporation. Averages of the results for these five tests are as follows: The theoretical maximum rate of evaporation was 1.77 g per

Table II. Rate of Evaporation of Zn in Relation to Power

| Number | Zn Evaporated from Crucible, G | Zn Condensate, G | Zn Accounted for by Level Difference | Power, Kw | Avg Rate of Evaporation, G per Sq Cm per Min |
|--------|--------------------------------|------------------|--------------------------------------|-----------|----------------------------------------------|
| 19     | 1542                           | 1523             | 1544                                 | 3.0       | 0.384                                        |
| 20     | 1629                           | 1610             | 1632                                 | 4.75      | 0.706                                        |
| 21     | 1910                           | 1905             | 1933                                 | 4.0       | 0.419                                        |
| 22     | 1276                           | 1264             | 1254                                 | 3.0       | 0.230                                        |
| 23     | 1927                           | 1907             | 1975                                 | 4.0       | 0.370                                        |
|        |                                |                  |                                      | 5.0       | 0.634                                        |
| 24     | 2186                           | 2173             | 2185                                 | 3.0       | 0.085                                        |
|        |                                |                  |                                      | 4.0       | 0.462                                        |
|        |                                |                  |                                      | 5.0       | 0.819                                        |



sq cm per min, and the observed rate was 0.577 g per sq cm per min, or 35 pct of the maximum. The average residual gas pressure was about 50 microns, and the zinc vapor near the surface was about 66 pct saturated.

### Temperature Gradient Near the Surface

The temperature of the metal at the surface, where evaporation is taking place, may be much cooler than the temperature of the main body of metal, as indicated by the crucible temperature. The difference between the crucible and surface temperatures is illustrated in Figs. 3 and 4. The difference is due to the cooling effect of rapid evaporation. The heat required to evaporate 1 g of zinc at 500°C is about 440 cal. The thermal conductivity of liquid zinc is 0.138 cal per sq cm per cm per sec per °C.<sup>4</sup> The temperature gradient required to evaporate  $W$  g of zinc per sq cm per min<sup>2</sup> is given by:

$$\frac{dt}{dx} = \frac{440 W}{60 \times 0.138} = 53W \quad [6]$$

This means that a temperature gradient of about 50°C per cm is required to evaporate zinc at a rate of 1 g per sq cm per min. The temperature distribution in the metal is determined by the flow of heat from the crucible walls and the adjacent metal where it is generated to the surface from which the metal is evaporated.

The surface-follower unit was used to measure the temperature gradient in the metal while evaporation was proceeding at a high rate. The follower automatically established the exact location of the surface as a reference while the thermocouple tube was manually adjusted. The results of this experiment are given in Fig. 8. The observed rate of evaporation as determined by the surface follower was 0.570 g per sq cm per min. The temperature

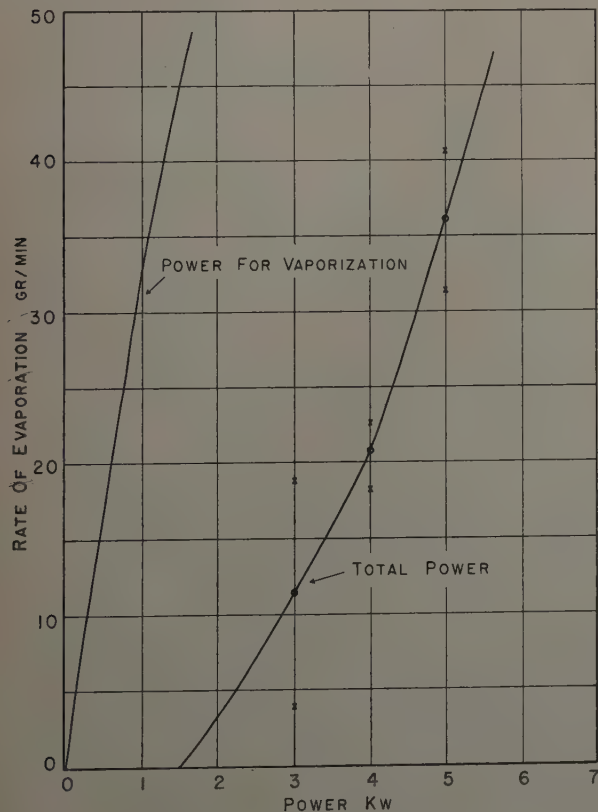


Fig. 7—Rate of evaporation vs. power.

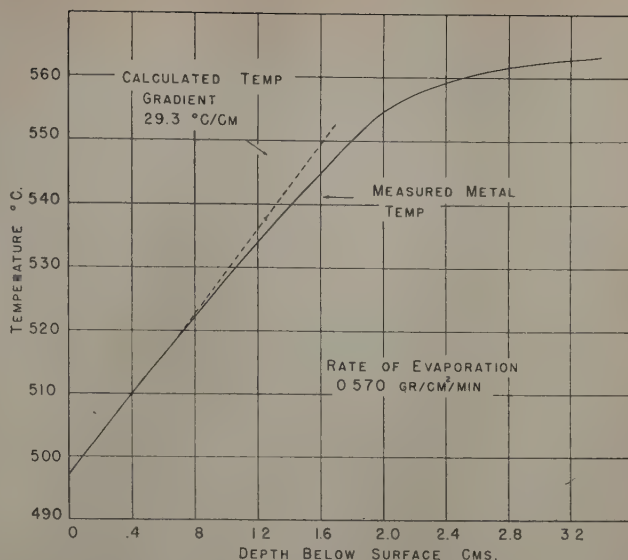


Fig. 8—Temperature distribution near surface of evaporating zinc.

of the metal at the surface was 497°C, for which the thermal conductivity is 0.1381 (cal per sq cm per cm per sec per °C). The calculated temperature gradient necessary to evaporate zinc at the observed rate would therefore be 29.3°C per cm. It will be observed that this value is in very close agreement with the measured gradient.

Previous gradient measurements<sup>2</sup> were made at lower rates of evaporation. At a rate of 0.264 g per sq cm per min, the gradient was calculated to be 13.85°C per cm, and it too was in fairly good agreement with the observed temperature distribution.

### Summary and Conclusions

By means of an automatic surface-follower mechanism, careful measurements were made of the surface temperature and rate of evaporation of molten zinc while undergoing evaporation at a rapid rate at very low pressures. At pressures of 50 to 100 microns, the rate of evaporation may be 60 to 80 pct of the maximum theoretical rate. As the pressure of the residual gas increases above 100 microns, the rate decreases; at a pressure of 2000 microns the observed rate of evaporation was only 7 pct of the theoretical rate corresponding to the observed surface temperature.

The surface temperature during rapid evaporation is much lower than the average temperature of the metal because of the large amount of heat abstracted from the surface by the evaporating molecules. Measurements of the temperature gradient at the surface were in good agreement with the theoretical gradient calculated from the heat of vaporization, rate of evaporation, and thermal conductivity of molten zinc.

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# Vapor Pressures of Zinc Over AgZn Alloys

by E. E. Underwood and B. L. Averbach

The vapor pressure of zinc in equilibrium with solid  $\beta$  AgZn alloys has been measured by the dew-point method. The thermodynamic activities of silver, and the molar heats of formation have been calculated. Similar measurements have been made for the ternary alloys formed by adding gold to AgZn. An apparent particle size effect has been observed for AgZn filings. The vapor pressure of zinc over filings is 15 to 20 pct higher than over the solid alloys.

STATISTICAL methods have been used to interpret the thermodynamic activities of the components of a solid solution in terms of average equilibrium atomic configurations. In some cases, the atomic arrangements can be measured by X-ray methods, and the results are usually expressed in terms of short range order parameters. Only in the cases of Cu<sub>3</sub>Au and AgAu have there been sufficient X-ray and thermodynamic data to verify the assumed correlation between the X-ray and the thermodynamic measurements. In Cu<sub>3</sub>Au the agreement is good; negative deviations from Raoult's law are observed and the number of Cu-Au nearest neighbor pairs predicted on the basis of the thermodynamic treatments agrees quite well with the number of such pairs observed by the X-ray methods.

The  $\beta$  brass alloys present a different set of conditions. The ordering is so rapid in these alloys that

the disordered state cannot be retained on quenching. In contrast, the disordered state in Cu<sub>3</sub>Au is easily retained on quenching. On heating, the ordered  $\beta$  brass loses its long range order continuously as the critical temperature is approached; in Cu<sub>3</sub>Au the order decreases slightly on heating and then drops discontinuously to zero at the critical temperature. These differences indicate that the short range order configurations in  $\beta$  brass systems may be of a different character than in Cu<sub>3</sub>Au systems. However, X-ray measurements of local order cannot be made in the Cu-Zn alloys because of the similarity in scattering factors. The alloy AgZn is isomorphous with CuZn, however, and recent experiments have indicated that there is a good possibility of observing short range order in this system.

Another complication arises in the case of  $\beta$  AgZn. The disordered body-centered cubic structure exists above 280°C. On quenching from above this temperature an ordered structure of the cesium-chloride type is formed. On slow cooling, however, a complex hexagonal structure, the  $\zeta$  phase, is produced; and if an ordered quenched alloy is reheated the  $\zeta$  phase begins to form above 80°C. It is thus difficult to study local order by X-ray methods in single crystals of AgZn since the  $\zeta$  phase formed on heating does not necessarily return to a single crystal of the original orientation. This problem has been met, however, by adding a few percent of gold to the AgZn. The gold suppresses the formation of the  $\zeta$

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phase, without otherwise altering the structure, and this made it possible for Muldawer<sup>7</sup> to study the long range order in  $\beta$  AgZn as a function of temperature.

Local order measurements are being undertaken in the gold-bearing  $\beta$  AgZn alloys. In order to investigate the correlation between thermodynamic activities and short range order, the vapor pressures of zinc in equilibrium with various alloys of  $\beta$  AgZn and  $\beta$  AgZn plus Au were measured. These thermodynamic data are reported in this paper.

Several attempts have been made to detect the excess free energy associated with the formation of new surfaces. These experiments have, in general, been unsuccessful, and there has been no direct experimental verification of the Thompson equation which relates the practical size with the excess free energy. In this paper the vapor pressure of zinc in equilibrium with fine filings of  $\beta$  AgZn was meas-

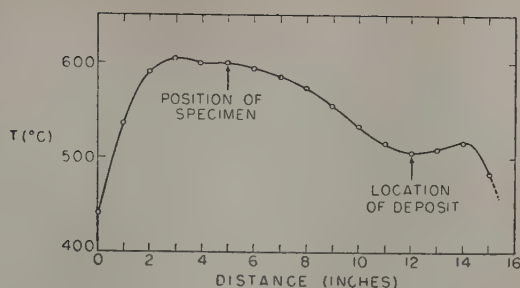


Fig. 2—Temperature gradient along furnace tube.

calibrated against a Bureau of Standards Pt-Pt-10 pct Rh thermocouple, were used.

The alloys were prepared from silver shot, more than 99.99 pct pure, and from zinc sticks of about 99.98 pct Zn; for the ternary alloys, gold of 99.96 pct purity was added. Melts were made in a graphite crucible in an induction furnace, and the crucible and melt were quenched into water to minimize segregation. The ingot was machined to a  $\frac{3}{4}$  in. diam cylinder and annealed in an evacuated tube at 640°C for several days. The  $\frac{3}{8}$  in. diam specimen was then prepared, thoroughly degreased, and sealed into the clear quartz tube.

Each specimen was held at temperature overnight in the quartz tube and observations were started on the following morning by lowering the temperature at the opposite end of the furnace. After the first deposit of liquid zinc droplets was observed, the temperature of the droplets was raised until they evaporated, then lowered slowly until they reappeared. This process was repeated until the equilibrium temperature was determined. At the higher vapor pressures the dew point could be determined within  $\pm 1^\circ\text{C}$ , but at lower pressures only within  $\pm 2^\circ\text{C}$ . Chemical analyses of the specimens before and after the dew-point determinations agreed closely and indicated that a negligible amount of zinc had been lost during the measurements.

It is believed that dezincification of the alloy surfaces did not occur to any noticeable extent. The vapor pressure measurements were performed at relatively high temperatures where the diffusion

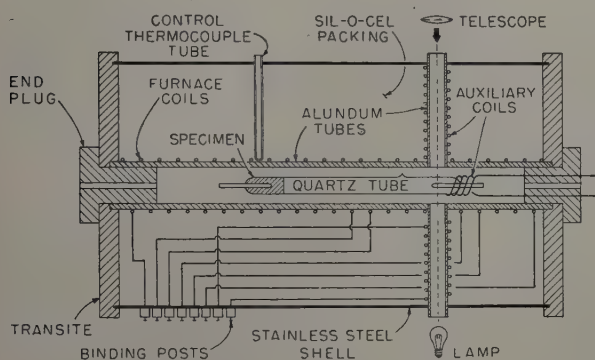


Fig. 1—Sketch of furnace cross-section.

ured and found to be measurably higher than the vapor pressure in equilibrium with a bulk sample of the same alloy. This excess vapor pressure was associated with the large local curvature present in the filings, although no experimental measurement of this local curvature was made.

### Experimental Method

The Hargreaves<sup>8</sup> dew-point method was used to measure the vapor pressure of zinc over solid alloys. In this method an alloy is placed at one end of an evacuated clear quartz tube which has a deep thermocouple well at each end and a side arm for evacuation and sealing. The sample was a  $\frac{3}{8}$  in. diam cylinder 1  $\frac{1}{16}$  in. long and contained a hole drilled into one end so that the sample could slip over the thermocouple well. The quartz tube was placed inside a tube furnace heated by three separately controlled resistance windings and so arranged that the end of the evacuated tube containing the alloy could be maintained at a constant temperature,  $T_h$ , while the temperature at the other end of the tube could be lowered to a selected temperature  $T_c$ . When  $T_c$  was below the dew point of the zinc vapor, droplets of liquid zinc were observed over the thermocouple well at the cold end, and the equilibrium value of  $T_c$  was taken as halfway between the closest temperatures of condensation and evaporation.

The furnace is shown schematically in Fig. 1 and a typical temperature gradient for this furnace is shown in Fig. 2. A small coil, independently controlled, was placed around the condensation end of the quartz tube for fine temperature control. The maximum fluctuation observed at the hot end of the tube was  $\pm 1^\circ\text{C}$ . Chromel-alumel thermocouples,

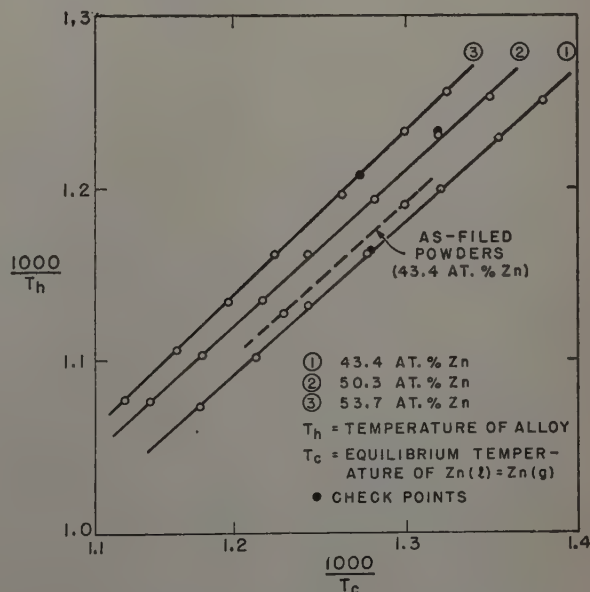


Fig. 3—Plot of  $\frac{1}{T_h}$  vs.  $\frac{1}{T_c}$  for binary alloys.

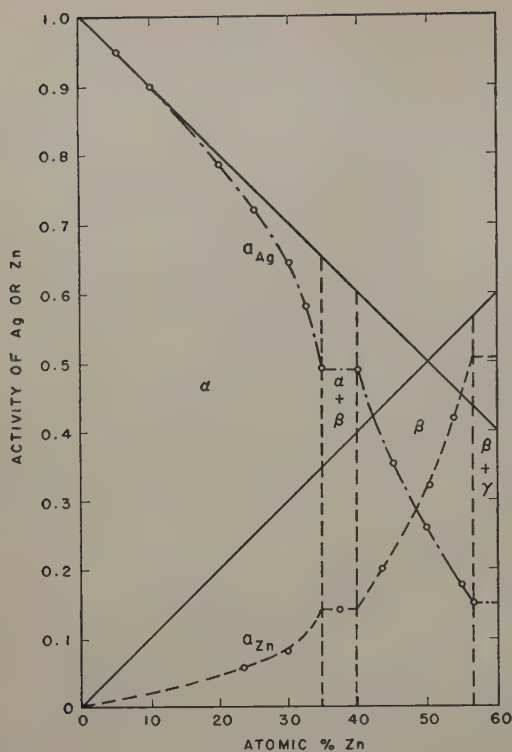


Fig. 4—Activities of silver and zinc in Ag-Zn alloys at 620°C. Activity of zinc referred to liquid zinc.

rates are quite large. In a closed system where no zinc is lost to the atmosphere, it would be expected that a steady state would be reached rather quickly and the specimen would attain a uniform composition.

The vapor pressure measurements were made on each sample at a series of temperatures. The experimental points shown in Fig. 3 were not taken in sequence and no systematic deviations of vapor pressure were noted during the long periods of time (10 to 14 days) during which the specimens were at temperature. Furthermore, the amount of zinc in the vapor phase is negligibly small. At the highest pressures encountered, about 0.001 g Zn would be in the vapor phase, while the weight of the sample was about 12 g.

In addition, check runs were made later with the same specimens, and the confirmation of the original data was quite satisfactory, see Fig. 3. Table I shows that the vapor pressures of zinc over the bulk alloys were the same, within experimental error, as those over the corresponding preheated powders. This would not be expected if dezincification had occurred. Finally, a comparison of the dew-point method for measuring vapor pressures over  $\alpha$  Cu-Zn alloys<sup>8</sup> with the absorption spectra method,<sup>9</sup> the weighing method,<sup>10</sup> and the carrier-gas method<sup>11</sup> shows the dew-point method to good advantage.

A one degree error in  $T_c$  was found to introduce a relative error of 2.5 pct in the activity of zinc. Deviations in chemical analyses averaged between 1 to 2 pct and the overall error was estimated at 5 to 10 pct.

### Experimental Results

The experimental values may be checked quickly for consistency by plotting  $\frac{1}{T_h}$  vs.  $\frac{1}{T_c}$ . If the vapor pressure throughout the tube is considered to be the

same, the Clausius-Clapeyron equation for each end may be written as:

$$\ln p = \frac{-\Delta H_v}{RT_h} + C = \frac{-\Delta H_v^\circ}{RT_c} + C' \quad [1]$$

where  $p$  is the zinc vapor pressure within the tube;  $\Delta H_v$  and  $\Delta H_v^\circ$  are the heats of vaporization of zinc from the alloy and from pure liquid zinc, respectively;  $R$ , the gas constant; and  $C$  and  $C'$ , the integration constants. If  $\Delta H_v$ ,  $\Delta H_v^\circ$ ,  $C$ , and  $C'$  are taken as independent of temperature:

$$\frac{1}{T_h} = K \cdot \frac{1}{T_c} + K' \quad [2]$$

Fig. 3 shows such a plot of the experimental temperatures with the best straight lines determined by the method of least squares. The vapor pressures for pure zinc were obtained from the equations of Kelley.<sup>3</sup> The activities and activity coefficients of zinc with respect to liquid zinc are listed in Table I. The activities of silver at three temperatures were calculated by means of the Gibbs-Duhem equation. The activities for zinc and silver at 620°C are shown in Fig. 4, and the activities of zinc are indicated on the Ag-Zn equilibrium diagram in Fig. 5.

Birchenall and Cheng<sup>4</sup> obtained only one point within the  $\beta$  field and this is somewhat lower than the corresponding value obtained in this investigation. However, the vapor pressure of one alloy in the  $\alpha$  region containing 31.3 atomic pct Zn was measured and showed good agreement with the Birchenall and Cheng data. These data, plus those of Schneider and Schmid<sup>5</sup> for liquid Ag-Zn alloys at 700°C, are shown in Fig. 6. The similarity to the data for solid alloys is quite striking. In order to compare the data for liquids with the data obtained in this research, the zinc activities for the solid alloys were extrapolated to the solidus at 700°C and compared with the corresponding value for the activity of the liquid in equilibrium with this composition. The activities (referred to liquid zinc) were 0.24 from the extrapolation of the solid values and 0.26 from the liquid data.

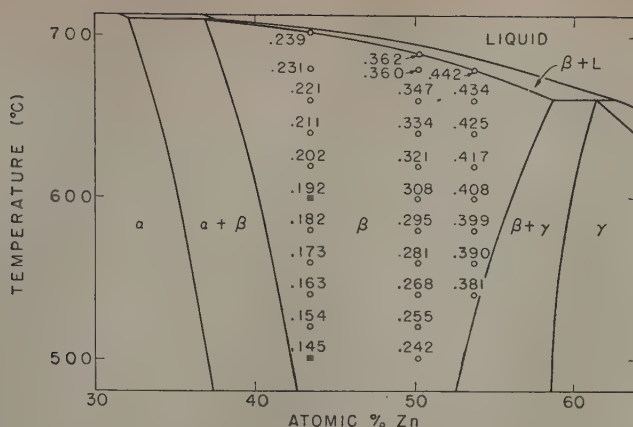
Partial molar heats of formation, relative to pure solid zinc or silver, were calculated for several com-

Table I. Activities of Zinc (referred to liquid zinc) in Various Alloys

|                                                     | Temperatures, °C |       |       |         |       |       |         |       |       |
|-----------------------------------------------------|------------------|-------|-------|---------|-------|-------|---------|-------|-------|
|                                                     | 500              | 520   | 540   | 560     | 580   | 600   | 620     | 640   | 660   |
| <b>Binary Alloys</b>                                |                  |       |       |         |       |       |         |       |       |
| 43.4 atomic pct Zn                                  | 0.145            | 0.154 | 0.163 | 0.173   | 0.182 | 0.192 | 0.202   | 0.211 | 0.221 |
| 50.3 atomic pct Zn                                  | 0.242            | 0.255 | 0.268 | 0.281   | 0.295 | 0.308 | 0.321   | 0.334 | 0.347 |
| 53.7 atomic pct Zn                                  | 0.361            | 0.371 | 0.381 | 0.390   | 0.399 | 0.408 | 0.417   | 0.425 | 0.434 |
| <b>Ternary Alloys</b>                               |                  |       |       |         |       |       |         |       |       |
| 43.9 atomic pct Zn (6.68 atomic pct Au)             | 0.131            | 0.140 | 0.149 | 0.158   | 0.166 | 0.175 | 0.185   | 0.194 | 0.204 |
| 47.8 atomic pct Zn (3.33 atomic pct Au)             | 0.167            | 0.176 | 0.187 | 0.196   | 0.208 | 0.217 | 0.227   | 0.238 | 0.249 |
| <b>Powders Filled and Preheated 2 days at 560°C</b> |                  |       |       |         |       |       |         |       |       |
| 43.4 atomic pct Zn                                  |                  |       |       | 0.161   | 0.170 | 0.179 | 0.189   | 0.197 | 0.207 |
| 50.9 atomic pct Zn                                  |                  |       |       | 0.270   | 0.282 | 0.295 | 0.305   | 0.318 | 0.342 |
| 53.4 atomic pct Zn                                  |                  |       |       | 0.360   | 0.373 | 0.385 | 0.396   | 0.409 | 0.432 |
| <b>As-filed Binary Powders</b>                      |                  |       |       |         |       |       |         |       |       |
| 43.4 atomic pct Zn                                  |                  |       |       | 567.9°C |       |       | 613.8°C |       |       |
|                                                     |                  |       |       | 0.204   |       |       | 0.236   |       |       |



Fig. 5—Activities of zinc on the Ag-Zn equilibrium diagram, referred to liquid zinc.



positions in the  $\beta$  field from the slopes of the straight lines obtained by plotting  $\ln a_{\text{Zn}}$  or  $\ln a_{\text{Ag}}$  vs.  $\frac{1}{T}$ . The relative integral molar heat of formation at the composition AgZn was approximately -1880 cal per mol and the corresponding partial molar heats were  $\Delta\bar{H}_{\text{Zn}} = -1590$  and  $\Delta\bar{H}_{\text{Ag}} = -2170$  cal per mol.

**Ternary Alloys:** The addition of 3 atomic pct Au to  $\beta$  AgZn alloys is sufficient to suppress the formation of the  $\zeta$  phase. The vapor pressure of zinc was measured for two alloys with 3.33 and 6.68 atomic pct Au and the data are summarized in Table I. The zinc vapor pressures of the two ternary alloys were less than those from corresponding binary

Table II. Vapor Pressure of Zinc over  $\beta$  AgZn Filings  
43.4 Atomic Pct Zn

| Temperature, °C | Vapor Pressure of Zn Over Filings, $p'$ (mm) | Vapor Pressure of Zn Over Bulk Alloy, $p$ (mm) | $\frac{p'}{p}$ |
|-----------------|----------------------------------------------|------------------------------------------------|----------------|
| 614             | 3.50                                         | 2.95                                           | 1.19           |
| 568             | 1.26                                         | 1.09                                           | 1.16           |

Ag-Zn alloys at the same temperature. Schneider and Schmid<sup>5</sup> showed that the activities of zinc in liquid Au-Zn alloys were lower than in Ag-Zn alloys. Hargreaves<sup>2</sup> measured the zinc vapor pressures over solid Ni-Cu-Zn alloys and also found a decrease in vapor pressure in comparison with the Cu-Zn alloys.

**Powdered Alloys:** Ag-Zn powders were prepared by filing from the same homogenized castings that were used to obtain specimens for the vapor pressure measurements. Clean files and a decreased vise were used, and iron fragments were removed with a permanent magnet. Only particles which would pass a 325 mesh screen were used. The powder was fed into one end of the cleaned quartz tube up to the point usually occupied by the solid specimens and packed as much as possible by tapping. After heating the as-filed particles, a light brown cloudy film appeared at the cold end of the tube but the liquid droplets could still be observed. Vapor pressure measurements were also made on filings which had been preheated at 560°C for two days. In these cases the brown film was not observed.

A significant increase in the vapor pressure was obtained over the as-filed powders in comparison with the bulk material. These differences have been summarized in Table II. The ratio of the zinc vapor

pressure over the filings,  $p'$ , to the pressure over the bulk alloys,  $p$ , is approximately 1.15 to 1.20.

According to the Thompson equation:

$$\ln \frac{p'}{p} = \frac{2\sigma \bar{V}}{RT\bar{r}}$$

where  $\sigma$  is the specific surface free energy;  $\bar{V}$ , the partial molar volume;  $R$ , the gas constant;  $T$ , the temperature; and  $\bar{r}$ , the effective radius of curvature. Assuming a value of 700 ergs per sq cm for  $\sigma$  at 800°K, the effective radius of curvature,  $\bar{r}$ , is calculated to be approximately 0.03 microns.

This effect can be explained in terms of the shapes of typical filings observed under the microscope. The filings contain many sharp, jagged edges and the net effect of such peaks could produce this increase in vapor pressure, provided that the effective radius of curvature was small enough and that the radius of curvature of the valleys was much larger. The valleys need not necessarily cancel the increase in pressure due to the peaks, unless the valleys had much the same (negative) radius of curvature. The sharp edges of the as-filed powders were found to be somewhat rounded off after the runs had been completed. However, it can be said that when sharp-edged particles were introduced into the furnace, higher vapor pressures resulted than when rounded particles were used initially.

The zinc vapor pressures of the filings preheated

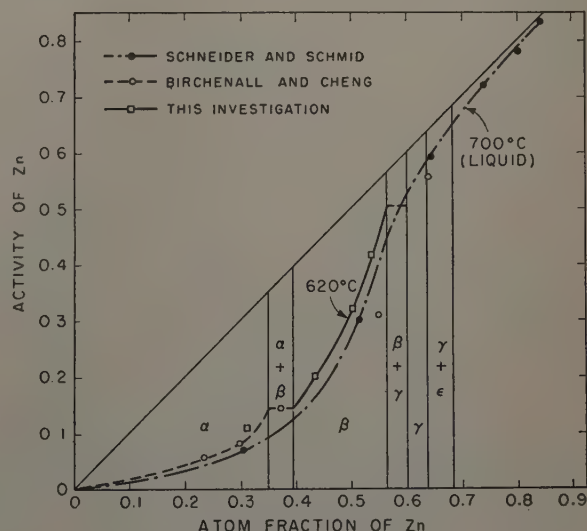


Fig. 6—Activity of zinc in Ag-Zn alloys, referred to liquid zinc.

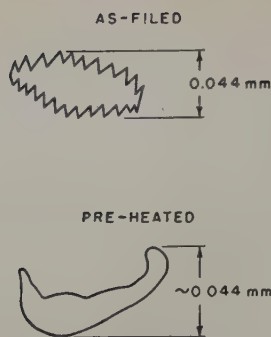


Fig. 7—Cross-sections of Ag-Zn filings.

for two days at 560°C were determined next. The activities of zinc for the preheated powders are essentially the same as those obtained for the corresponding bulk alloys and the values are listed in Table I. A metallographic examination of these preheated powders showed that the jagged edges had been rounded off approximately as shown in Fig. 7.

Neither powder showed any appreciable evidence of sintering as a result of the heating incidental to the vapor pressure measurements. Chemical analyses of the filings after the runs checked closely with the original analyses.

### Discussion of Results

A correlation between the measured activity coefficients and the corresponding equilibrium atomic arrangement can only be made in an approximate fashion. As a starting point it may be assumed that the entropy of mixing for zinc and silver atoms in the body-centered cubic solution is ideal and the heat of mixing may be interpreted in terms of nearest neighbor interactions. For a regular solution it can be shown<sup>8</sup> that:

$$\frac{ZN_{\nu}(1 - X_A)^2}{RT} = \ln \gamma_A \quad [4]$$

where  $Z$  is the number of nearest neighbors,  $N_{\nu}$ , Avogadro's number;  $X_A$ , the atomic fraction of component A;  $\gamma_A$ , the activity coefficient of component A; and  $\nu = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$ , the interaction energy. This equation only applies to the case where the activity coefficients are referred to a pure metal A which has the same crystal structure as the alloy. However, in the  $\beta$  AgZn region, the activities of the zinc in the body-centered cubic alloy have been referred to the pure solid metal in the hexagonal close-packed form. A straightforward calculation of the interaction energy from the measured activity coefficients thus contains a structural contribution from the hypothetical phase change Zn(hexagonal close-packed) = Zn(body-centered cubic).

The activities for the 50.3 atomic pct Zn alloy were calculated with respect to solid zinc as a standard state and these values were used to evaluate  $\nu$ . On

plotting  $\ln \gamma_{zn}$  as a function of  $\frac{1}{T}$  a straight line was

obtained and the slope of this line gave a value of -790 cal per mol for  $N_{\nu}$ . Cowley<sup>7</sup> has derived an approximate relationship for  $\beta$  brass structures between the interaction energy  $\nu$  and  $T_c$ , the critical temperature for long range order:

$$\frac{N_{\nu}}{R} = \frac{-T_c}{4} \quad [5]$$

Recently the long range order was measured by Muldawer<sup>1</sup> in several ternary AgZn plus Au alloys. On extrapolating the critical temperatures to binary AgZn, a value of 270°C was obtained for  $T_c$ . This corresponds to -275 cal for  $N_{\nu}$ . The difference, -515 cal per mol, may be assigned to the hypothetical phase change Zn(hexagonal close-packed) = Zn(body-centered cubic). This value, however, cannot be verified experimentally.

It is difficult to reconcile the apparent higher vapor pressures observed over the filings in terms of a particle size effect alone. The 15 to 20 pct increase in vapor pressure corresponds to a local curvature of 0.03 microns, but the classical Thompson equation may not be valid for particles with such small radii of curvature. It is quite possible that surface contamination or the greatly disturbed surface due to the filing operation also contributed to the effect on vapor pressure.

### Summary

The thermodynamic activities in three solid  $\beta$  Ag-Zn alloys have been obtained over a temperature range of 500° to 660°C. The activities of silver and the molar heats of formation have been computed. Similar measurements have also been made for ternary AgZn-plus Au alloys.

An apparent particle size effect has been observed in the case of AgZn filings. The vapor pressures of zinc over -325 mesh filings were 15 to 20 pct higher than over solid alloys.

### Acknowledgments

The chemical analyses were performed by W. M. Saunders and D. L. Guernsey. The advice and assistance of L. L. Seigle and D. A. Hay are also gratefully acknowledged.

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# Analytical Representation of Certain Phase Boundaries

by W. Rostoker

Using an expression for the free energy of a homogeneous phase as a function of composition, a relationship is derived which interrelates the phase boundaries extending from the allotropic transformation of the solvent metal. Comparisons between observed and calculated phase boundaries in the systems Fe-Ni, Fe-Mn, Fe-W, Ti-Mo, and Ti-Cb are presented.

IT is the purpose of this paper to illustrate how the general free energy equations for two phases in equilibrium may be used to derive an expression which interrelates the phase boundaries extending from the allotropic transformation of the solvent metal. The free energy per gram atom of a disordered solid solution may, for many purposes, be represented by the equation:<sup>1</sup>

$$F = \frac{1}{2}NZ [C \cdot V_{AA} + (1-C) V_{BB} + 2C(1-C)V] + K(T) + RT [C \cdot \ln C + (1-C) \ln(1-C)] \quad [1]$$

where  $N$  is Avogadro's number;  $Z$ , the coordination number;  $C$ , the concentration of the solute element in atomic percent; the subscripts refer to concentrations at phase mixture boundaries;  $V_{AA}$ ,  $V_{BB}$ , and  $V_{AB}$  are the bond energies between like and unlike adjacent atoms, respectively, at the interatomic spacing characteristic of the phase. The bond energies are usually assumed to be independent of small changes in the lattice parameter occasioned by solute additions and variations in temperature;  $V = V_{AB}$

$$- \frac{V_{AA} + V_{BB}}{2}; K(T) \text{ is the sum of the heat con-}$$

tent and heat entropy;  $R$ , the molar gas constant; and  $T$ , the temperature in degrees Kelvin.

The free energy of a homogeneous phase is there-

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fore the sum of an internal energy, a specific heat, and a configurational entropy term, respectively. The compositions of two phases in equilibrium at a given temperature are governed by the minimum total free energy principle. Graphically, this is represented by the points of tangency of the tangent common to the free energy vs. concentration curves of the two phases.

Analytically, this may be expressed as:

$$\left( \frac{dF}{dc} \right)_\alpha = \left( \frac{dF}{dc} \right)_\beta \quad [2]$$

Expanding both sides using eq 1, the following equation is obtained after convenient readjustment of the terms:

$$RT \ln \left[ \left( \frac{C_\beta}{1-C_\beta} \right) \left( \frac{1-C_\alpha}{C_\alpha} \right) \right] = \frac{1}{2}N \frac{(V_{AA} - V_{BB})(Z_\alpha - Z_\beta) + NV}{[Z_\alpha(1-2C_\alpha) - Z_\beta(1-2C_\beta)]} \quad [3]$$

The following assumptions have been made at this point:

1—The specific heats of the two phases are independent of composition variations within the range under consideration. Accordingly, the  $K(T)$  terms disappear on differentiation.

$$2—(V_{AA})_\alpha = (V_{AA})_\beta; (V_{BB})_\alpha = (V_{BB})_\beta; V_\alpha = V_\beta$$

The justification for these assumptions can lie only in the successful application of the resultant equation. It may be noted that Zener<sup>2</sup> has used assumption 1 in the calculation of the boundaries limiting the  $(\alpha+\beta)$  phase mixture in the Cu-Zn system.

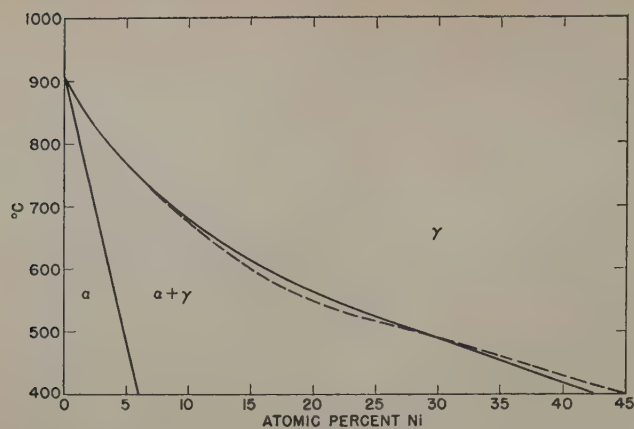


Fig. 1—Calculated, dashed line, and observed,<sup>8</sup> solid line, boundaries in the Fe-Ni system.

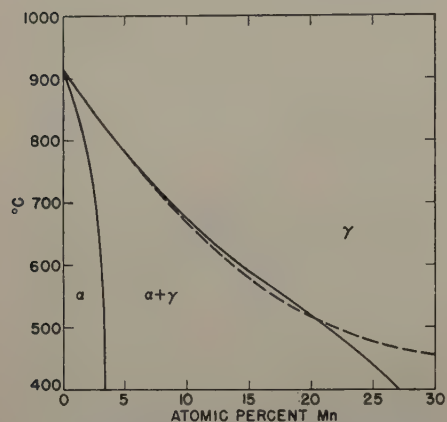


Fig. 2—Calculated, dashed line, and observed,<sup>6</sup> solid line, boundaries in the Fe-Mn system.

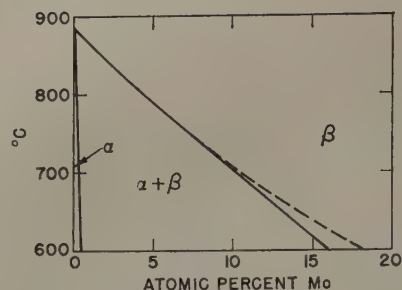


Fig. 3—Calculated, dashed line, and observed,<sup>8</sup> solid line, boundaries in the Ti-Mo system.

Eq 3 may be reduced to a more simplified form:

$$RT \ln \left[ \left( \frac{C_\beta}{1-C_\beta} \right) \left( \frac{1-C_\alpha}{C_\alpha} \right) \right] = K_1 [Z_\alpha - Z_\beta] + K_2 [Z_\alpha(1-2C_\alpha) - Z_\beta(1-2C_\beta)] \quad [4]$$

where  $K_1 = \frac{1}{2}N(V_{AA} - V_{BB})$  and  $K_2 = NV$ . The values of the constants may be calculated from reliable data for  $C_\alpha$ ,  $C_\beta$  at two temperatures. Eq 4 has been applied to several cases of phase mixture boundaries extending from the allotropic transformations of pure iron. Recent work on certain titanium-rich systems has permitted additional interesting examinations of the above relationship.

In the Fe-Ni system, the composition of the rejected  $\alpha$  phase is isothermally invariant with time and consequently the accurate experimental location of the  $\alpha/(\alpha+\gamma)$  boundary is much less difficult than the corresponding  $(\alpha+\gamma)/\gamma$  boundary of the phase mixture. Using the data for the  $\alpha/(\alpha+\gamma)$  boundary and two reliable values of  $C_\gamma(T)$ , the whole  $(\alpha+\gamma)/\gamma$  boundary may be calculated by successive graphical solutions of eq 4.

The calculation for the Fe-Ni system may be summarized as follows: Using data from Owen and

Sully,<sup>8</sup> constants  $K_1$  and  $K_2$  were evaluated as  $K_1 = 703$  and  $K_2 = 140$ . Eq 4 becomes (since  $Z_\alpha = 8$  and  $Z_\gamma = 12$ ):

$$RT \ln \left[ \left( \frac{C_\gamma}{1-C_\gamma} \right) \left( \frac{1-C_\alpha}{C_\alpha} \right) \right] = 2248 + 1128 \frac{[3C_\gamma - 2C_\alpha]}{[3C_\gamma - 2C_\alpha]}$$

The value of  $C_\gamma$  corresponding to a given  $C_\alpha$  may be found from the intersection of curves of:

$$RT \ln \left[ \left( \frac{C_\gamma}{1-C_\gamma} \right) \left( \frac{1-C_\alpha}{C_\alpha} \right) \right] \text{ vs. } C_\gamma$$

$$2248 + 1128 [3C_\gamma - 2C_\alpha] \text{ vs. } C_\gamma$$

Fig. 1 shows a good agreement between calculated and experimental boundaries.

Similar calculations have been applied to the same type of phase boundaries found in the systems Fe-Mn, Ti-Mo, and Ti-Cb. The results are graphically represented in Figs. 2, 3, and 4, respectively. Fig. 5 shows that the same treatment may be applied to the closed  $\gamma$  loop of the Fe-W system. The constants for the equations are summarized in Table I. It will be seen that the assumptions regarding the independence from composition of certain free

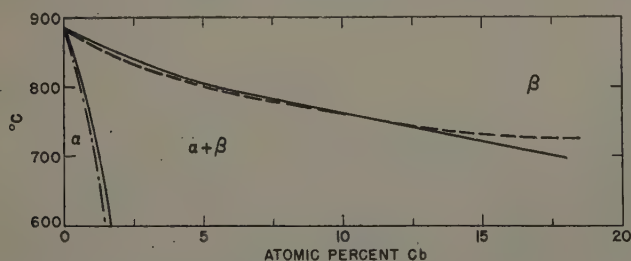


Fig. 4—Calculated, dashed line, adjusted, dash-dot line, and observed,<sup>8</sup> solid line, boundaries in the Ti-Cb system.



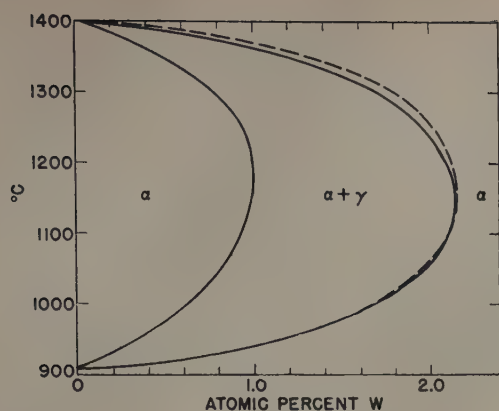


Fig. 5—Calculated, dashed line, and observed,<sup>7</sup> solid line, boundaries in the Fe-W system.

energy terms is valid in several cases for solute concentrations of as much as 30 atomic pct.

A useful application of this analytical method arose in the study of the phase boundaries for the titanium-rich Ti-Cb system. The  $\alpha/(\alpha+\beta)$  boundary was first drawn as the best fit between brackets established by micrographic analysis at various temperatures. Using points from this boundary to calculate the  $(\alpha+\beta)/\beta$  boundary yielded results widely divergent from the experimental work. By trial and error, it was found that a reasonable corroboration could be obtained if the  $\alpha/(\alpha+\beta)$  boundary was redrawn in a new position which also lay within the confines of the brackets imposed by the data. It is suggested that eq 4 may be applied to experimental phase boundaries as a check of self-consistency.

It will be noted that the constant  $K_1$  is represented as the difference between two terms which embody the molar cohesive energies of the pure components divided each by the coordination number. Using published data for molar cohesive energies<sup>4</sup> and the coordination number of the high temperature allotropic modification, calculated values for  $K_1$  are presented in Table I for comparison with the observed values. For example, the calculation of  $K_1$  for the Fe-Ni system proceeds as follows:

$$K_1 = \frac{1}{2} N (V_{\text{Fe-Fe}} - V_{\text{Ni-Ni}}) =$$

$$\left[ \frac{\text{molar cohesive energy of Fe}}{12} - \frac{\text{molar cohesive energy of Ni}}{12} \right]$$

$$= \left[ \frac{94000}{12} - \frac{85000}{12} \right]$$

$$= 750 \text{ cal}$$

The agreement in general is quite good, considering that no temperature corrections were made and that the published data pertains to cohesive energies at

Table I. Summary of Constants

| System | $K_1$   | $K_2$ | $K_1$ (As Calculated from Eq 4) |
|--------|---------|-------|---------------------------------|
| Fe-Ni  | +703    | +140  | +750                            |
| Fe-Mn  | +1535   | +257  | +1670                           |
| Fe-W   | -16,250 | -9500 | -18,410                         |
| Ti-Mo  | +5085   | -448  | +7500                           |
| Ti-Cb  | -4050   | +2700 | -4000                           |

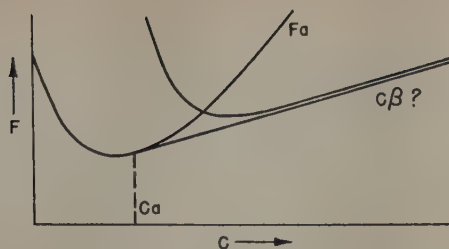


Fig. 6—Hypothetical free energy vs. concentration curves illustrating a possible origin of the indeterminate location of a phase boundary.

the interatomic spacings of the pure metals, rather than their acquired spacings in solid solution.

The calculated  $(\alpha+\gamma)/\gamma$  boundary of the Fe-Ni system tends towards parallelism with the abscissa in the composition range which has always been the most difficult to study. The same effect may be noted in the cases of the Fe-Mn, Ti-Mo, and Ti-Cb systems (see Figs. 2, 3, and 4). This trend could be due to a breakdown of the assumptions upon which eq 4 are founded. On the other hand, the same effect could arise if the free energy vs. composition curve for the  $\gamma$  or  $\beta$  phase became approximately linear such that no unique tangent could be drawn. This is diagrammatically shown in Fig. 6. An examination of free energy data obtained by Kubaschewski and v. Goldbeck<sup>5</sup> indicate that this condition is possible.

There seems to be sufficient evidence that phase boundaries of the types considered can be represented by an equation derived from fundamental free energy relationships but involving certain ad hoc assumptions. An attempt to treat the  $(\alpha+\beta)$  boundaries of the Cu-Zn system by the same method met with no success. This mention should serve to emphasize that eq 4 has limited application.

A much more elaborate development of this subject along classical thermodynamic lines has been published by Zener.<sup>9</sup> The writer feels justified in presenting this alternative treatment because of its greater simplicity and because the results, while not as widely applied, are at least as closely in agreement with experimental data.

### Acknowledgment

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# Surface Tension of Solid Silver

by E. R. Funk, H. Udin, and J. Wulff

The surface tension of solid silver is measured by a refinement of the Udin, Shaler, and Wulff technique. The tests were made in a purified helium atmosphere at four different temperatures and various times. The average of the results is  $\gamma = 1140 \pm 90$  dynes per cm for the range  $875^\circ$  to  $932^\circ\text{C}$ .

A SUCCESSFUL measurement of the surface tension of solid copper was reported by Udin, Shaler, and Wulff.<sup>1</sup> They performed experiments on copper held in vacuum within  $100^\circ\text{C}$  of the melting point. At these temperatures, the creep rate in 5 and 3 mil copper wires was sufficient to permit determination of a balance between the contractile force

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of surface tension and the extending force of small copper weights joined to the end of the wire specimens. By suspending a series of variously weighted specimens and measuring the change in a gage length during the test, the balancing applied load could be found. This point of zero strain is a measure of the surface tension. The mathematical formulation of this gives:

$$w = \pi r \gamma \quad [1]$$

where  $w$  is the weight for zero strain;  $r$ , the radius of the wire; and  $\gamma$ , the surface tension.

A subsequent note by Udin<sup>2</sup> pointed out that eq 1 applies only to single-crystal specimens. Since the specimens used revealed a "bamboo" structure upon

Table I. Applied Stress and Resulting Strain for Each Specimen

| Test No.   | 22                      |                        | 23                      |                        | 24                      |                        | 25                      |                        | 26                      |                        |
|------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|
| Spec. No.* | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ |
| 1          | 0.68                    | -83                    | 0.66                    | -181                   | 0.69                    | -36                    | 0.60                    | -58                    | 0.56                    | -63                    |
| 2          | 1.01                    | -43                    | Specimen damaged        |                        | 1.11                    | -49                    | 0.87                    | -57                    | 1.07                    | -74                    |
| 3          | 1.39                    | -41                    | 1.36                    | -44                    | 1.41                    | -44                    | 1.31                    | 6                      | 1.33                    | -12                    |
| 4          | 1.71                    | 56                     | 1.70                    | 46                     | 1.71                    | 42                     | 1.64                    | 17                     | 1.67                    | 28                     |
| 5          | 2.18                    | 61                     | 2.18                    | 122                    | 2.24                    | 48                     | 2.11                    | -8                     | 2.15                    | 45                     |
| 6          | 2.95                    | 181                    | 2.92                    | 211                    | 2.93                    | 72                     | 1.96                    | 30                     | 2.88                    | 121                    |
| 7          | 3.53                    | 216                    | 3.37                    | 417                    | 3.48                    | 29                     | 3.31                    | 43                     | 3.45                    | 96                     |
| 8          | 4.10                    | 298                    | 4.10                    | 328                    | 4.06                    | 148                    | 4.03                    | 34                     | 4.03                    | 120                    |
| 9          | 4.79                    | 383                    | 4.80                    | 457                    | 4.67                    | 170                    | 4.62                    | 32                     | 4.65                    | 71                     |
| 10         | 5.73                    | 413                    | 5.67                    | 652                    | 5.90                    | 311                    | 5.63                    | 119                    | 5.77                    | 232                    |
| 11         | 8.49                    | 626                    |                         |                        | 9.02                    | 534                    | 8.44                    | 288                    | 8.93                    | 475                    |
| 13         |                         |                        |                         |                        | 0.10                    | -93                    | 0.09                    | -40                    | 0.08                    | -88                    |
| 14         | 0.11                    | -154                   | 0.12                    | -187                   | 0.09                    | -70                    | 0.08                    | -76                    | 0.09                    | -52                    |

\* Specimens numbered according to the position occupied in the cell cover.



metallographic examination, the equation must be modified to take into account the grain boundary energy. Since the grain boundaries are perpendicular to the axis of the wire, eq 1 becomes:

$$w = \pi r \gamma - \left(\frac{n}{l}\right) \pi r^2 \gamma_{gb}$$
 [2]

where  $\gamma_{gb}$  is the interfacial tension of a grain boundary and  $n/l$ , the number of grains per unit length.

Greenough<sup>3</sup> has shown, and further experiments in this laboratory have confirmed, that for silver in an inert atmosphere, the grain boundary interfacial tension for the average grain boundary is one third the tension of the free surface. Therefore eq 2 may be rewritten as:

$$w = \pi r \gamma \left[1 - \frac{n}{l} \frac{r}{3}\right]$$
 [3]

For the special case of the wires in our experiments  $n/l$  is  $60 \pm 10$  grains per cm and  $r$  is 0.0065 cm, so that the equation relating the surface tension to the balancing load for polycrystalline wires is then:

$$w = \pi r \gamma [0.87]$$
 [4]

The applied stress for zero strain is the balancing load divided by the cross-sectional area of the wire:

$$\gamma = \frac{\sigma_{\epsilon=0} r}{0.87}$$
 [5]

where  $\sigma_{\epsilon=0}$  is the applied stress for zero strain.

Experimental Procedure

The techniques used by Udin, Shaler, and Wulff were used in modified form to measure the surface tension of solid silver. The wire was 0.00508 in. in diam and was drawn from a billet of high purity, vacuum cast silver. Preliminary experiments showed that commercially available fine silver wire was not suitable for this work because uninhibited grain growth did not occur, presumably due to the presence of oxides or other inclusions.

Two gage marks were cut into the wire approximately 1 cm apart so that the strain in the specimens could be measured. These marks were made by rotating the wire against the edges of spaced razor blades in an especially designed machine.<sup>4</sup> Each end weight, prepared from a length of the silver wire, was melted on a charcoal block and the end of the wire thrust into the molten ball as it solidified. In all the runs, 10 to 13 wires were used with external end weights ranging from 0 to 120 mg.

The wires were suspended from a silver cell cover

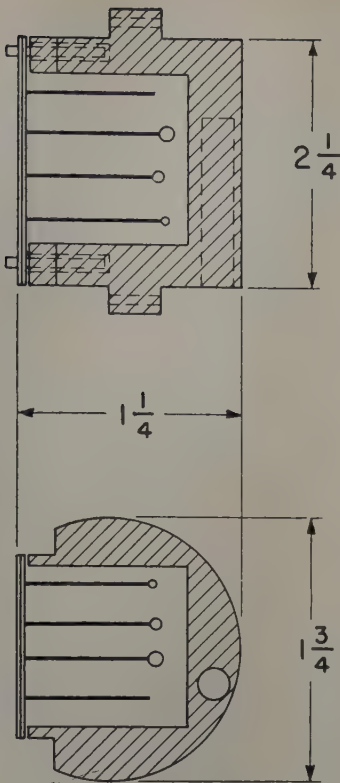


Fig. 1—Silver cell with thermocouple well.

and then the array was carefully transferred to a silver cell. The cover closed but did not seal the cell. The cell, shown in Fig. 1, was then transferred to a platinum wound Inconel tube furnace. This furnace has been described elsewhere.<sup>1</sup>

Preliminary runs were carried out in a vacuum of  $5 \times 10^{-6}$  mm Hg, but the evaporation of the silver wires at the test temperatures was so rapid that no reproducible results could be obtained. The runs reported here were therefore carried out in a purified helium atmosphere. A helium flow of 3 cu cm per sec was maintained in the furnace throughout the run. The helium was purified by passing it through an activated charcoal trap held at liquid nitrogen temperatures.

Due to the manipulation required for mounting, the wires were often slightly bent and cold worked. An anneal treatment of a few minutes at 600°C was sufficient to allow straightening of the wires.

The specimens were washed in alcohol and ether

Table I. (Continued)

| Test No.  | 27                      |                        | 28                      |                        | 30                      |                        | 31                      |                        | 32                      |                        |
|-----------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|
| Spec. No. | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ | $\sigma \times 10^{-5}$ | $\epsilon \times 10^5$ |
| 1         | 0.47                    | -83                    | 0.52                    | -90                    | 0.54                    | -57                    | 0.64                    | -61                    | 0.55                    | -159                   |
| 2         | 0.84                    | -35                    | 1.08                    | -66                    | 1.09                    | -23                    | 0.80                    | -31                    | 0.79                    | -69                    |
| 3         | 1.32                    | -7                     | 1.32                    | -56                    | 1.31                    | 25                     | 1.27                    | -27                    | 1.31                    | -11                    |
| 4         | Specimen damaged        |                        | 1.53                    | 61                     | 1.63                    | 51                     | 1.47                    | 8                      | 1.63                    | 32                     |
| 5         |                         |                        | 2.14                    | 80                     | 0.08                    | -86                    | 1.97                    | 60                     | 2.16                    | 71                     |
| 6         | Specimen damaged        |                        | 2.93                    | 200                    | 2.92                    | 115                    | 2.62                    | 120                    | 2.94                    | 250                    |
| 7         | 3.27                    | 143                    | 3.41                    | 285                    | 3.42                    | 196                    | 3.78                    | 182                    | 3.42                    | 332                    |
| 8         | Specimen damaged        |                        | 4.04                    | 323                    | 4.03                    | 262                    | 4.02                    | 259                    | 4.02                    | 433                    |
| 9         | 4.59                    | 172                    | 4.65                    | 172                    | 4.62                    | 350                    | 4.36                    | 264                    | 4.64                    | 429                    |
| 10        | 5.55                    | 344                    | 5.78                    | 277                    | 5.88                    | 705                    | 5.47                    | 411                    | 5.80                    | 695                    |
| 11        | 8.40                    | 417                    | 8.89                    | 1047                   | 8.91                    | 784                    | 8.26                    | 641                    | 8.89                    | 1078                   |
| 12        |                         |                        |                         |                        |                         |                        | 0.10                    | -99                    |                         |                        |
| 13        |                         |                        |                         |                        | 0.09                    | -122                   |                         |                        |                         |                        |
| 14        | 0.07                    | -131                   | 0.09                    | -319                   | 0.09                    | -166                   |                         |                        |                         |                        |
| 16        |                         |                        |                         |                        |                         |                        | 0.09                    | -125                   | 0.10                    | -201                   |

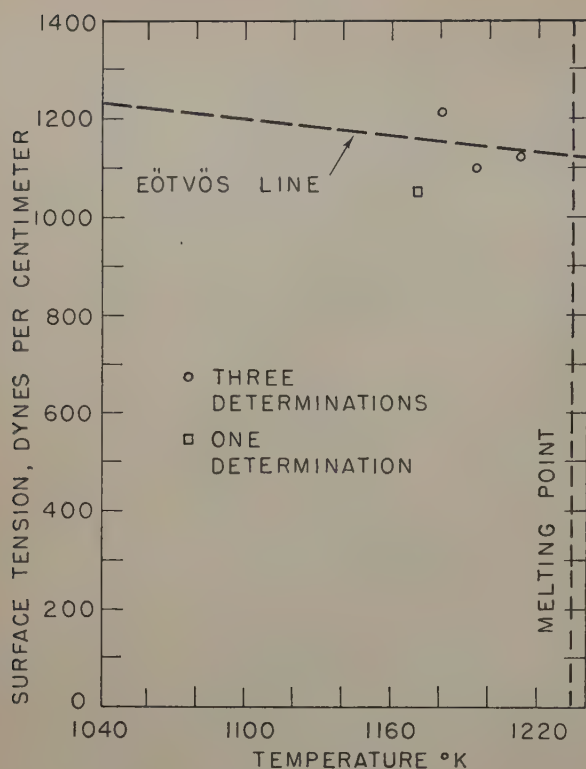


Fig. 2—Temperature dependence of the surface tension of solid silver.

to remove dirt and returned to the furnace for a high temperature anneal. This anneal lasted 1 hr at 940°C. The specimens were removed from the furnace after cooling, and the gage length of each wire was measured with a vertical traveling microscope with a screw accurate to  $\pm 0.00015$  cm. This array was returned to the furnace for the run which lasted up to 116 hr for the lower temperatures and as short as 18 hr for the higher temperatures. Upon cooling the wires were removed from the furnace and the gage lengths again measured. The weights were clipped off at the weld and weighed to  $\pm 0.1$  mg.

It was always possible to count the number of grains in each wire after a test was completed. This is possible because an equilibrium of surface forces exists where the grain boundary meets the free surface. The groove angle established at the grain boundary<sup>3, 4</sup> is distinctly visible under diffuse oblique illumination at X50. These grooves are often visible even after the short 940°C anneal. A grain count on a number of specimens after the anneal and also after the test itself showed that the grain size established during the anneal remains essentially unchanged.

Table II. Summary of Experimental Results

| Test No. | Test Temperature, °C ( $\pm 1^\circ\text{C}$ ) | Duration of Test, Hr | Surface Tension, Dynes per Cm |
|----------|------------------------------------------------|----------------------|-------------------------------|
| 22       | 938                                            | 18                   | 1110                          |
| 23       | 941                                            | 29                   | 1150                          |
| 24       | 923                                            | 18                   | 1190                          |
| 25       | 906                                            | 26                   | 1265                          |
| 26       | 923                                            | 36                   | 1115                          |
| 27       | 907                                            | 50                   | 1210                          |
| 28       | 907                                            | 108                  | 1215                          |
| 29       | Run lost                                       |                      |                               |
| 30       | 924                                            | 64.5                 | 1005                          |
| 31       | 876                                            | 116                  | 1045                          |
| 32       | 938                                            | 59.5                 | 1070                          |

The surface tension for all runs was calculated from eq 5. A straight line fits the data for applied stress between 0 and  $4 \times 10^5$  dynes per sq cm. Points of larger applied stress were not included in the calculation. A least square calculation was used to determine the most probable stress at zero strain. The necessary but small ( $0.15 \times 10^5$  dynes per sq cm) correction to the ball weight for the weight of the wires between the lower gage mark and the weight was also made.

The values for the applied stress and the resulting strain for each specimen in each successful run are given in Table I. A summary of the experimental results is presented in Table II.

## Discussion and Conclusions

Ten tests for the surface tension of solid silver in a purified helium atmosphere were made at four different temperatures and various times. The average of the results is  $\gamma = 1140 \pm 90$  dynes per cm for the range 875° to 932°C. There is a tendency for short time runs to give slightly higher values for surface tension than runs of long duration. This trend seems to occur at all the test temperatures but is, in general, less than the experimental error. If it is a real phenomena, it may be attributable to one of several reasons. There may be a gradual adsorption of traces of metallic vapor contaminant. More likely, the average diameter of the wires decreases due to evaporation. This decrease would not have been detected if it was less than  $5 \times 10^{-5}$  in., and such a decrease would lead to a decrease of some 20 to 40 dynes per cm in the apparent value of the surface tension.

Fig. 2 shows the temperature dependence of the surface tension. In spite of the scatter of the data, probably attributable in a large part to the high sensitivity of silver to gaseous contamination, a least square calculation of the ten tests gives a temperature coefficient of  $-0.47$  dynes per cm of °K. This is in good agreement with the coefficient theoretically predicted by the Eötvös rule. This rule says that the surface tension of a liquid decreases linearly to zero at the critical temperature. Assuming a critical temperature of 3330°K and, correcting for a liquid-solid interfacial tension of 200 dynes per cm,<sup>6, 7</sup> the Eötvös rule coefficient is  $-0.45$  dynes per cm per °K. It is assumed that Antonow's rule holds at the melting point so that the sum of the liquid-vapor surface tension and the liquid-solid surface tension equals the solid-vapor surface tension.

## Acknowledgment

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# Surface Tension of Solid Gold

by F. H. Buttner, H. Udin, and J. Wulff

Using a modified Udin, Shaler, and Wulff technique, the surface tension of gold in purified helium was found to be  $1400 \pm 65$  dynes per cm for the temperature range  $1017^\circ$  to  $1042^\circ\text{C}$ .

IN the original Udin, Shaler, and Wulff technique for measuring the surface tension of copper,<sup>1</sup> variably weighted wires were allowed to extend or contract in a copper cell held at elevated temperatures in vacuum. By plotting stress vs. strain for a wire array in one test, the stress at zero strain is obtained. This is the point where the contractile forces resulting from surface tension are balanced by the applied load, according to the expression:

$$\gamma = \sigma_{\epsilon=0} r \quad [1]$$

where  $\gamma$  is the surface tension in dynes per cm;  $\sigma_{\epsilon=0}$ , the stress at zero strain in dynes per cm; and  $r$ , the radius of the wire in cm. The assumption that the wires deform viscously permits the drawing of a straight line through the points on the stress-strain plot. Justification of the assumption has received further experimental support recently.<sup>2-4</sup>

The presence of grain boundaries in the wires requires a correction to the original expression used.<sup>5</sup> Thus:

$$\gamma = \sigma_{\epsilon=0} \cdot r [1 - (n/l)(ar)]^{-1} \quad [2]$$

where,  $n/l$  is the number of grain boundaries per unit length, and  $a$ , the ratio of grain boundary tension to free surface tension.

Alexander, Kuczynski, and Dawson<sup>3</sup> in studying the creep of gold wire in vacuum were unable to obtain reproducible values of the surface tension of gold. In plotting stress vs. strain for progressively longer times, they found that the stress at zero strain drifted with time from positive stress values to negative values. Similarly, for the surface tension of silver, reproducible values were obtained only when a purified helium atmosphere was substituted.<sup>2</sup> Evidently the evaporation rate of silver in vacuum is too high at the temperatures employed to obtain solid-gas equilibrium even in a similar metal enclosure. Thus reproducibility of results is lost.

## Experimental Procedure

The experimental procedure was much the same as that originally developed by Udin, Shaler, and Wulff with a few modifications and improvements. For greater accuracy in strain measurements, knots gave way to cut gage marks as shown in Fig. 1. These were made with a hand-driven lathe in which

razor blades served as cutting tools. Also a more precise cathetometer with a screw accurate to 0.00015 cm was used. The tests were conducted in an atmosphere of purified helium rather than in vacuum in order to avoid possible evaporation difficulties. Five mil wire of high purity gold (99.98 pct) was used.

After cutting in the gage marks, each wire of a series of about 12 was differently loaded by welding a gold ball to one end. This was done by dipping the end of the wire in a cooling gold droplet, previously melted on a charcoal block with a No. 2 acetylene torch. The other end of the wire was strung through a hole in a gold lid and twisted over the edge to hold the wires fixed and in suspension from the lid. The lid and mounted wires were then dipped in pure ethyl alcohol to dissolve any skin oils and dirt on the surface of the wires due to handling. Finally the lid was put in place on an alundum crucible lined with gold so that the wires hung freely within the gold-lined chamber. This whole assembly was next heated in a quartz nichrome wound tube furnace and heated for a few minutes at  $600^\circ\text{C}$  to soften the wires. After this anneal the wires were easily straightened with tweezers.

The wire assembly was finally annealed  $10^\circ$  to  $25^\circ\text{C}$  above the subsequent test temperature for 2 hr. This treatment allowed the grains to grow to equilibrium size and shape. After the anneal, the lid was mounted in front of the cathetometer. The gage length was measured by sighting the 40 power microscope on the upper lip of the lower gage mark for the first reading, then traveling up to the lower lip of the upper gage mark for the final reading. This procedure was repeated four times to give an average gage length value. In this manner the annealed gage length and the final gage length could be measured to determine the strains. During all measurements, grain counts were made.

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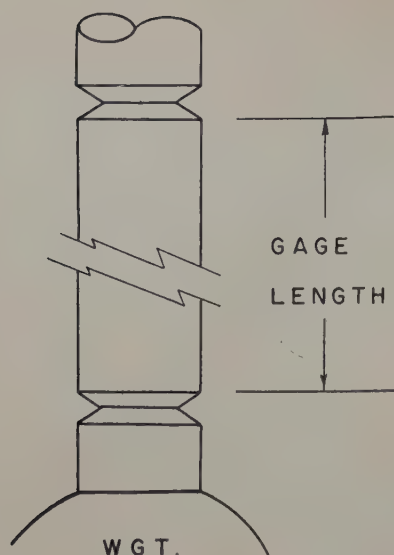


Fig. 1—Loaded wire with cut gage marks.

The furnace used was an 18 in. quartz tube, 2 7/8 in. diam, wound with three nichrome tapered windings each controlled through a separate rheostat. The temperature was held to  $\pm 1^\circ\text{C}$  over the 4 in. hot zone by a Celestray temperature controller. Two thermocouples, one for the temperature controller and the other a traveling thermocouple, were used to check the temperature distribution over the length of the furnace. The helium used as furnace atmosphere was passed through an activated charcoal trap held in liquid nitrogen. A getter boat containing titanium powder was also kept in the hot zone of the furnace. This last precaution was shown by run No. 5 to be unnecessary.

Nine tests were made in purified helium, while

one test, No. 5, was carried out in air. The results of these tests are compiled in Table I, and shown graphically in Fig. 2. After a least square analysis of the data, the surface tension was calculated using eq 1. From these results the corrected surface tension was obtained with the aid of eq 2.

### Discussion and Conclusions

Test No. 5, run in air, gave a lower surface tension value than the tests run in helium. The result is however not sufficiently suppressed to indicate that oxygen adsorption is important as is the case in silver.<sup>4</sup> The short duration of run No. 9 at the lowest temperature exhibits so high a percentage of error that it was discarded.

The average value for the apparent surface tension was found to be  $1250 \pm 50$  dynes per cm over the range  $1280^\circ$  to  $1315^\circ\text{K}$ . For the corrected value, eq 2 was used, where  $n/l = 75$ , and  $a = 0.300$ , which together give a correction factor of 0.889. The average corrected value over the same range of temperatures then becomes  $1400 \pm 65$  dynes per cm. The value for  $n/l$  was computed from the average grain count with respect to the average annealed gage length of ten randomly chosen wires. The value for the constant,  $a$ , was computed from the average grain boundary angle for 250 readings by the reflected light method of Greenough and King<sup>6</sup> where the grain boundary angle averaged  $163^\circ$ .

The least square line drawn through the points of Fig. 2 has a slope of  $-0.433$ , which is in fair agreement with the Eötvös slope of  $-0.354$ . For silver<sup>2</sup> much closer agreement obtains.

### Structure of the Gold Wires

The wires were of the typical bamboo or reed-like structures observed before.<sup>1-3,7</sup> An excellent series of micrographs of gold wires appear in a paper by Alexander, Dawson, and Kling,<sup>7</sup> showing kinking, offsetting, and what appears to be bulging. Similar effects were observed in the experiments reported here.

The phenomena of kinking and offsetting is critically discussed by Herring,<sup>8</sup> who predicts this behavior on the basis of his theoretical treatment. Kinking appears to be the result of rotation of the grains about an axis lying in the grain boundaries. Offsetting, which is seen only in heavily loaded wires, results from the normal viscous behavior of grain boundaries.

Concerning the matter of bulging, Zener<sup>9</sup> has shown theoretically that the surface tension forces in wires of this type should cause each wire to break up into a series of small connected spheres. Alexander, Dawson, and Kling conclusively demonstrated the reality of Zener's prediction by heating for 120 hr a gold wire lying in an alundum boat at  $1055^\circ\text{C}$ . It is thought that if this tendency is appreciable under the conditions of the experiments, accordingly appreciable error might be expected in the final results. As a matter of fact, Alexander, Dawson, and Kling attribute some erratic behavior in lightly loaded wires in their experiments to this phenomenon.

In the experiments reported here as well as those reported by Funk, Udin, and Wulff, dummy wires were attached to and never removed from the same lid used throughout all the tests. Some of the dummy wires were plastically strained so as to introduce artificial bulges at the restrained region of the grain boundaries, and waists at the regions of no restraint in the middle of grains. These dummy

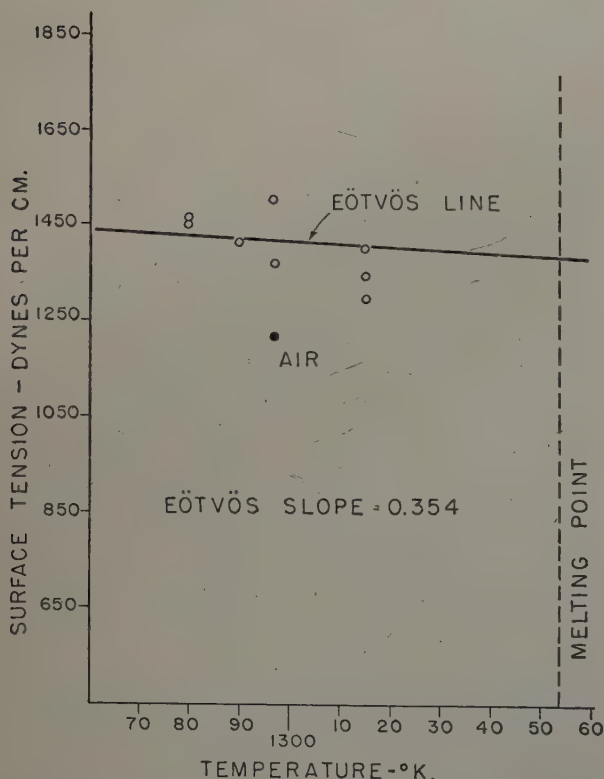


Fig. 2—Average surface tension vs. temperature  $^\circ\text{K}$  showing Eotvos line.



wires accumulated at least 200 hr under the exact test conditions of these experiments. In no case was a visible incipient breakup in the unstrained wires observed nor was an aggravation of the bulged condition of the strained wires seen. Cut gage marks also introduce a start toward the expected breakup of the wires. But actually here the opposite effect is observed in that the gage marks over a period of time at the test temperatures tend to disappear by smoothing over.

Apparent bulges appear in mounted and polished specimens. A plane section as formed by polishing through a kink produces what appears to be a sizeable bulge as shown in the line drawing of Fig. 3. Also bulges may appear on polished specimens due to strains introduced by mounting the specimens in bakelite.

Even if bulges were to exist, they may not exert as strong an influence as might at first be thought. If it is assumed for the moment that the wires do change into what might be called an idealized string of small spheres, or series of waists and bulges, and if it is also assumed that the idealized condition evolves by removing a ring of material from the cylinder to form a waist, and then putting it back on the cylinder slightly above the waist to form a bulge—by doing this all along the wire a contoured bulge and waist condition is created. In this process, no elongation or contraction is effected. Comparing the strain of a contoured wire to a cylindrical wire after a period of time at the test temperature, excessive elongation at the waists will be offset by deficient elongation at the bulges. Thus, the overall elongation of the contoured shape should be the same as a uniform elongating cylinder. The sum of the vertical components of surface tension over the contoured surface equals the vertical tension of the original cylindrical surface. Thus, in this idealized condition, no difference in important behavior can be found from that of a cylindrical wire.

Although there is no reason to believe that the wires will assume the idealized condition, nevertheless any bulge and waist model would necessarily be some approach to the ideal. Only the departure of the actual from the ideal would introduce error into the results of the experiments.

The tendency of the wires to spheroidize is observed to be vanishingly small for the configuration of experiment described here. Visible beginnings of spheroidization would in themselves introduce only second-order errors, insofar as they depart from the above idealized picture. Thus, any errors due to a

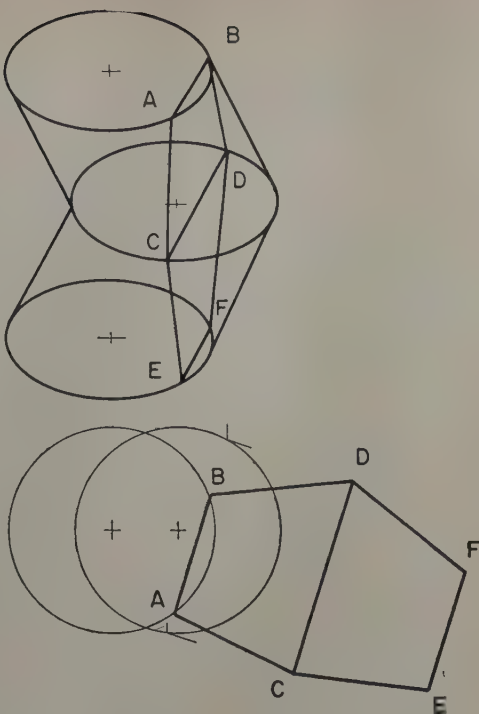


Fig. 3—Construction of the polished surface cutting through a kink.

tendency to bulge are lost in the normal experimental uncertainties of the technique.

Summary

Using a modified Udin, Shaler, and Wulff technique the surface tension of gold in purified helium was found to be  $1250 \pm 50$  dynes per cm. Using the Udin correction for grain boundary energy, this becomes  $1400 \pm 65$  dynes per cm for temperature range  $1280^\circ$  to  $1315^\circ\text{K}$ .

It has been observed that no spherical breakup of the wires is present in these experiments. Bulges appear on polished specimens, but this appears to be a spurious effect of the mounting and polishing technique. Ideas are presented indicating that the experiments could be carried out to the beginnings of visible spheroidization without introducing a significant error in either the value of surface tension or the rate of axial creep.

Acknowledgments

The authors wish to acknowledge their indebtedness to the Office of Naval Research for equipment and supplies purchased under contract number N5ori-07841, and to E. R. Funk for his assistance in carrying out the experimental work.

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Table I. Thermal History and Results of Each Run

| Run No. | Temperature °K (± 1°K) | Time, Hr | Dynes per Sq Cm x10 <sup>5</sup> | Apparent Surface Tension, Dynes per Cm | Corrected Surface Tension, Dynes per Cm | Precision of Correction |
|---------|------------------------|----------|----------------------------------|----------------------------------------|-----------------------------------------|-------------------------|
| 1       | 1315                   | 23.5     | 1.845                            | 1190                                   | 1340                                    | ± 77                    |
| 2       | 1297                   | 18.0     | 1.882                            | 1214                                   | 1367                                    | ± 53                    |
| 3       | 1280                   | 36.0     | 2.016                            | 1300                                   | 1464                                    | ± 55                    |
| 4       | 1315                   | 31.5     | 1.779                            | 1148                                   | 1293                                    | ± 40                    |
| 5*      | 1297                   | 36.0     | 1.660                            | 1072                                   | 1207                                    | ± 75                    |
| 6       | 1290                   | 36.0     | 1.940                            | 1252                                   | 1410                                    | ± 61                    |
| 7       | 1315                   | 9.0      | 1.923                            | 1240                                   | 1396                                    | ± 64                    |
| 8       | 1297                   | 10.5     | 2.078                            | 1334                                   | 1500                                    | ±118                    |
| 9       | 1280                   | 10.5     | 2.405                            | 1552                                   |                                         | ±158                    |
| 10      | 1280                   | 60.0     | 1.993                            | 1286                                   | 1448                                    | ± 35                    |

\* Run No. 5 made in air, all other runs in purified helium.

## Eutectoid Decomposition of the Delta Phase of the Copper-Tin System

by C. C. Wang and M. Hansen

THE  $\delta$  phase of the Cu-Sn system ( $\text{Cu}_{31}\text{Sn}_8 = 32.53$  pct Sn) was considered to be stable down to room temperature until Owen and Iball<sup>1</sup> showed by X-ray analysis that it undergoes a eutectoid decomposition into the  $\alpha$  and  $\epsilon$  phases at a temperature near 300°C. Their findings have been confirmed by other investigators,<sup>2-5</sup> all of whom used X-ray diffraction studies of powdered specimens. The transformation temperature has been reported by various authors as lying between 300° and 380°C. To our knowledge, no microscopic evidence of the eutectoid reaction has been published, as yet.

It was in connection with other work that long-time annealings at 300°C were conducted with alloys containing 22, 32.6, and 35 pct Sn (nominal compositions) prepared from electrolytic copper and electrolytic tin and cast in a small iron mold. The specimens were first annealed at 700°C for 5½ hr and quenched from 400°C after cooling to, and annealing at, that temperature for 9½ hr. After this

annealed 32.6 pct alloy, which was intended to consist entirely of  $\delta$  phase. Due to some loss in copper on melting, the composition is slightly higher in tin. Accordingly, the sample after quenching from 400°C consisted of grains of the  $\delta$  phase with the  $\epsilon$  phase arranged along the grain boundaries and as a Widmanstätten precipitate within the  $\delta$  grains. After an annealing time of 63 days, the eutectoid decomposition,  $\delta \rightarrow \alpha + \epsilon$ , is still in its early, initial state. The pearlitic type of eutectoid is nucleated at the  $\epsilon$  crystals, preferably those surrounding the grain boundaries of the  $\delta$  phase. The appearance of the  $(\alpha + \epsilon)$ -eutectoid in the 35 pct Sn alloy was very similar to that shown in Figs. 2 and 3. Again, the eutectoid decomposition nucleated at the  $\epsilon$  phase and proceeded from there into the  $\delta$  areas.

As is evident from Fig. 2, the rate of decomposition of the  $\delta$  phase at 300°C is extremely sluggish: In the representative area shown only about 5 pct of the  $\delta$  phase has undergone the eutectoid trans-

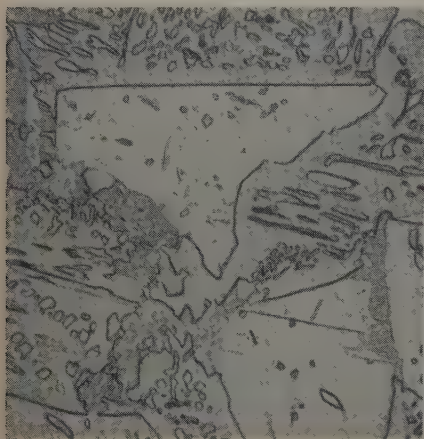


Fig. 1—About 22 pct Sn. X750.

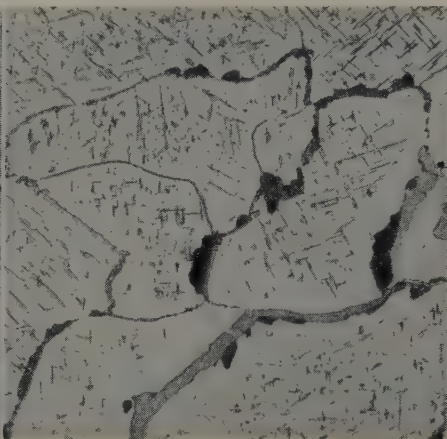


Fig. 2—About 33 pct Sn. X100.

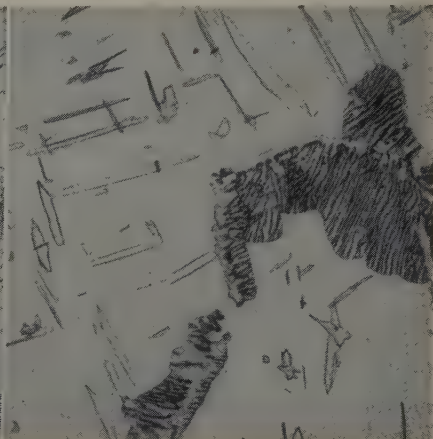


Fig. 3—About 33 pct Sn. X500.

Figs. 1 to 3—Microstructure of Cu-Sn alloys after annealing for 63 days at 300°C. Etchant,  $\text{FeCl}_3$ .

treatment the sample with 22 pct Sn was cold worked for 15 pct reduction in thickness; the 32.6 and 35 pct alloys were too brittle to be cold worked. The final anneal at 300°C was done in a sealed pyrex glass bulb for 63 days.

Fig. 1 represents the microstructure of the annealed alloy with 22 pct Sn. It shows primary  $\alpha$  solid-solution crystals in a matrix of the  $(\alpha + \delta)$ -eutectoid formed at 520°C. The  $\alpha$  crystals contain  $\delta$  inclusions which precipitated from  $\alpha$  due to the decrease in the solubility of tin in copper with fall in temperature. The decomposition of the  $\delta$  phase into  $\alpha$  (light) and  $\epsilon$  (dark) can clearly be seen in some areas of the  $(\alpha + \delta)$ -eutectoid matrix. However, the decomposition is far from being completed, even after the long-time anneal used.

Figs. 2 and 3 depict the microstructures of the

formation after annealing for 63 days. On the other hand, Owen and Williams<sup>2</sup> have reported that X-ray photographs of powdered samples with between 17.5 and 34 pct Sn did not show  $\delta$  lines after annealing for only five to seven days at 300°C. This is in accordance with the fact that the rate of reaction in powdered samples is higher than in massive specimens, as a result of the excess free energy of the powder (due to its greater surface area).

The authors wish to express their thanks to C. A. Johnson for preparation of the micrographs.

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C. C. WANG is associated with Massachusetts Institute of Technology, Cambridge, Mass., and M. HANSEN is with Armour Research Foundation of Illinois Institute of Technology, Chicago. TN 94E. Manuscript, Sept. 17, 1951.



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